September 1951 Pages 329 - 356

# The Journal
## *of the*
# SOCIETY OF DYERS AND COLOURISTS

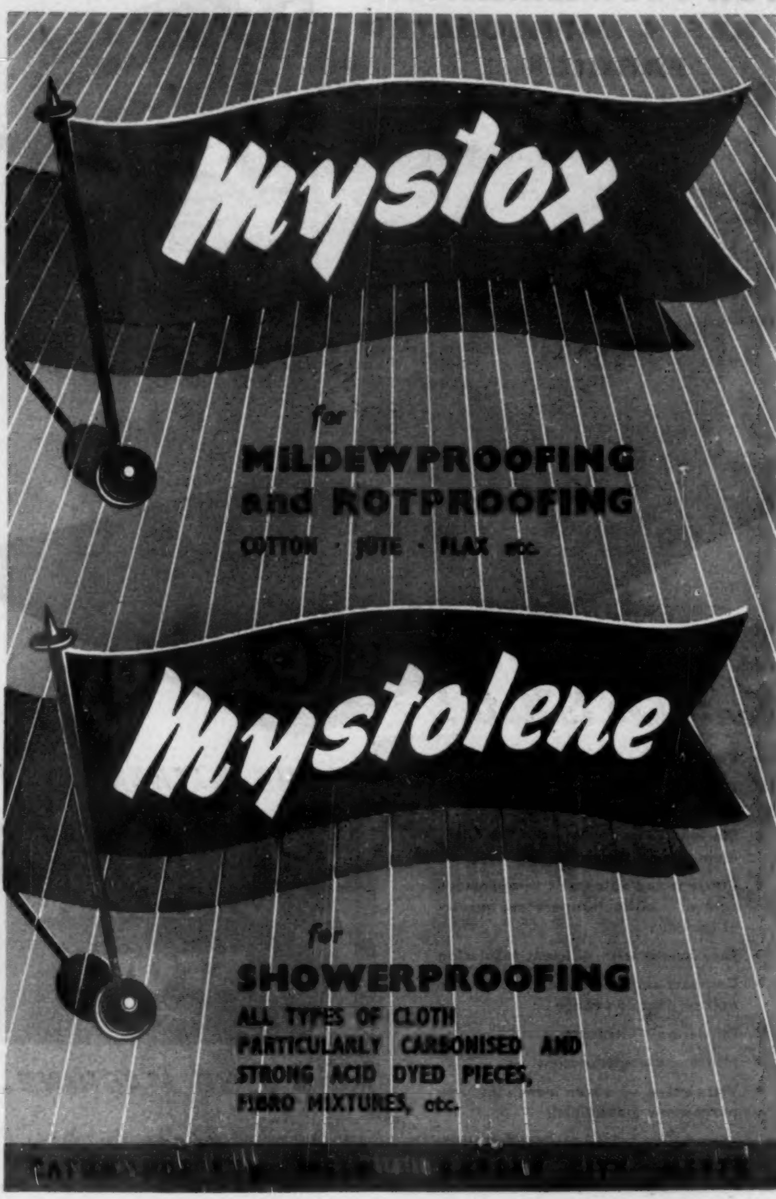
Volume 67 Number 9

CONTENTS



THE SOCIETY OF DYERS AND COLOURISTS 32-34 PICCADILLY BRADFORD YORKS


A COMPANY OF THE
PEGG
MELLOR BROMLEY GROUP
Dyeing & Finishing Machines
LOOSE STOCK DYEING MACHINE
For all types of loose wool and other loose stock. Built in stainless steel in two capacities, 100/250 lbs and 200/600 lbs.
LIGHT TYPE CALENDER
For finishing light-weight circular knitted fabrics, particularly interlock. Handles widths up to 35in.
PULSATOR HANK DYEING MACHINE
Stainless steel construction. Dyes all classes of wool, worsted mixture and linen yarns. Capacities from 50 to 1,500 lbs.
HEAVY TYPE CALENDER
Finishes circular knitted fabrics in wool, silk, cotton, rayon or mixture, in widths up to 36in.
YORKSHIRE PIECE GOODS DYEING MACHINE
For dyeing heavy or medium woollen or worsted piece goods in rope form. Built in stainless steel in three sizes.
DRYING AND FINISHING MACHINE
For drying and finishing all
SILK TYPE DYEING MACHINE
rope form. Four capacities, stainless steel.
POWER FABRIC LOADER
Speeds up loading and unloading between skips and dyeing machines, scouring machines, hydros etc. Eliminates dirty fabric.
PACKAGE DYEING MACHINE
Constructed in stainless steel in four sizes from single package samples to 488-package model.
PRE-BOARDING MACHINE
For shaping full fashioned or seamless nylon hose.
ROTARY DYEING MACHINE
Stainless steel construction in 25,50,100 and 200 lbs capacities
BROMAC FINISHING MACHINE
Imparts luxury finish to circular knitted fabrics. Automatic — built in one size for fabrics up to 33in. finished width.
OVAL TYPE PADDLE DYEING MACHINE
For dyeing hose, garments, hats and loose articles. Built in stainless steel in three sizes.
THREE BED PRESS
SAMUEL PEGG & SON LEICESTER
Office and Works—Barkby Road, Leicester Telephone 28196 Telegrams—Pulsator
8P14


Mystox
for
MILDEWPROOFING
and ROTPROOFING
COTTON · JUTE · FLAX etc.
Mystolene
for
SHOWERPROOFING
ALL TYPES OF CLOTH
PARTICULARLY CARBONISED AND
STRONG ACID DYED PIECES,
FIBRO MIXTURES, etc.

# The Journal of the Society of Dyers and Colourists

(Subscription rates for non-members 60/- per annum, post-free)
(Abstracts section only printed on one side of paper— 20/- per annum)

**NOTICE TO MEMBERS AND SUBSCRIBERS**

**Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1951 and pages 253–256 of the July 1951 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, 32–34 Piccadilly, Bradford, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.**

## Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

### LECTURES

Rayon Staple— A Dyeing Miscellany — *J. Boulton*

Causes of Unlevel Dyeing of Cotton Threads — *I. Gailey*

Recent Developments in Fluorescent Lamps, with Particular Regard to Colour Problems — *S. T. Henderson*

### COMMUNICATIONS

Advances in the Application of Vat Dyes to Viscose Rayon Cakes — *H. Hampson*

The Colorimetric Determination of Indigo — *J. Lotichius and J. Kooyman*

The Removal of Impurities from Grey Cotton. I— A Review of Developments in Plant for Alkali Boiling — *H. A. Turner and O. J. Hvattum*

## MEMBERS AND JUNIOR MEMBERS

***Persons desirous of joining the Society as Members, Associates, or Junior Members may obtain Application Forms from the General Secretary, or from the Honorary Secretary of any Section of the Society***

**NEW MEMBERS**

Adamson, G. A., Lurgan Hand Printing Co. Ltd., Lurgan, Co. Armagh, Northern Ireland
Bruce, D. W., The Airds, Bennett Road, Higher Crumpsall, Manchester 8
Coles, G. H., 66 Elmwood Crescent, Luton, Beds.
Durrans, G. A., Blamires Ltd., Leeds Road, Huddersfield
Grime, Miss S. M., 21 Brackley Road, Monton Green, Eccles, Manchester
Knight, F. J., c/o Hubbard Felt Co. Ltd., 425 Marien Avenue, Montreal East, P.Q., Quebec, Canada
Knight, J. W., 19 Park Avenue, Cheadle Hulme, Cheshire
Landreth, T. F., c/o Bruce Woollen Mfg. Co. Ltd., P.O. Box 2, Milton, Otago, New Zealand
Moucka, L., 10 Lisbarnett Villas, Lisbane, Co. Down, Northern Ireland
Sjoklint, E. G. R., Boras Wafveri AB, Boras, Switzerland
Stevens, N. E., Edenhurst, Alexandra Park, Nottingham

**JUNIOR MEMBERS**

Brooke, R., 8 College Road, Gildersome, near Leeds
Heaton, S., 10 Lapage Terrace, Bradford Moor, Bradford

## ADDRESSES WANTED

Breitfield, E., formerly of 16 Heathway Court, Childs Hill, Finchley Road, London N.W.3
Gifford, J. M., formerly of 86 Newlands Road, Glasgow
Gibbons, J. A., formerly of 98 Aberdale Gardens, Potters Bar, Middlesex
Justice, A., formerly of 35 Cumberland Avenue, Liverpool
Kulkarni, V. S., formerly of Kirparam Mehtas St., Gapipura, Surat, India
Kupczyk, J., formerly of 310 Dennam Street, Radford, Nottingham
Leman, R., formerly of 12 Ballerat Street, Levenshulme, Manchester 19
Mrozuik, J. S., formerly of 121 Glenfield Road, Leicester
Popper, E. D., formerly of Ballyrillan House, Belfast, N. Ireland
Presbury, J., formerly of 7 Sparthfield Avenue, Rochdale, Lancs.
de Franca Pereira, F. A., formerly of Rua Presidente Wilson, No. 6–4° – Dt, Lisboa, Portugal
Robinson, J., formerly of Glendene, Mavis Road, Blackburn
Sakari, K. B., formerly of 32 Khetwadi Main Road, Bombay 4, India
Selby, W., formerly of "Westwood", Woodhead Road, Stanningley, near Leeds
Srinivasan, V. R. (Dr.), formerly of c/o Bangalore Woollen, Cotton & Silk Mills Co. Ltd., Bangalore City, South India

# Fortheoming Meetings of the Society

1951
Thursday 25th Oct. PERKIN MEDAL LECTURE—Professor J. B. Speakman, Great Northern Hotel, Bradford

*Saturdays—20th October to 24th November 1951*
Leicester College of Technology and Commerce School of Chemistry The Newarke, Leicester
REFRESHER COURSE FOR DYERS
Arranged in collaboration with the Midlands Section of the Society of Dyers and Colourists

## LONDON SECTION

*All meetings held at 6 p.m. in the Rooms of the Royal Society, Burlington House, Piccadilly, London W.1, unless otherwise stated*

1951

Friday 5th Oct. F. Parrott, Esq. (C.A.C.). *The Colouring of Paper*

Friday 2nd Nov. W. S. Wood, Esq. and Dr. K. W. Richardson (Laporte Chemicals Ltd.). *Recent Developments in Bleaching with Hydrogen Peroxide*

Friday 7th Dec. G. S. J. White, Esq. (I.C.I.). *Recent Developments in Dyes and Colouring*

1952

Friday 4th Jan. J. E. Wood, Esq. and W. J. Roff, Esq. (B.C.I.R.A.). *The Identification of Synthetic Fibres, New and Old*

Friday 1st Feb. N. Jackson, Esq. (Courtaulds). *Faults and Damages in Fabrics*

Friday 7th Mar. Three short papers followed by a questionnaire on *Problems of the Garment Dyer and Cleaner*

It is also intended to hold a Dinner and Dance in the New Year, and to arrange for a lecture to be given in Luton in the spring, on a subject of interest to the hat industry. The date for the Annual General Meeting will be fixed later, for some time shortly after the last meeting of the session.

## MANCHESTER SECTION

1951

Friday 19th Oct. R. H. Peters, Esq. and W. J. Marshall, Esq. *The Reduction Properties of Vat Dyes.* Gas Showrooms, Town Hall Extension, Manchester at 6.30 p.m.

Thursday 1st Nov. (At the invitation of the Plastics Institute, North-Western Section). Professor W. T. Astbury. *Synthetic Fibres, Past and Present.* Manchester College of Technology

Friday 9th Nov. A lecture will be held at Bury. The details of which will be announced later

Friday 23rd Nov. Ladies' Evening, *Man as a Spider*, details to be announced later. Manchester College of Technology. 7 p.m.

Friday 21st Dec. (Joint with the British Association of Managers of Textile Works), discussion on Dyeing Machinery, introduced by F. H. Marsh, Esq. (Longclose Engineering Co. Ltd.), Midland Hotel, Manchester. 7 p.m.

1952

Friday 18th Jan. Details to be announced later, Gas Showrooms, Town Hall Extension, Manchester at 6.30 p.m.

Friday 15th Feb. E. H. Waters, Esq. and H. Sumner, Esq. *The Effect of Soaping of Vat Dyes.* Gas Showrooms, Town Hall Extension, Manchester. 6.30 p.m.

Thursday 6th March (Joint with the Textile Institute, Lancashire Section), Mr. Landolt. *Modern Developments in Textile Auxiliaries.* Textile Institute. 7 p.m.

Friday 21st March Symposium on *Systems of Pack Dyeing.* Gas Showrooms, Town Hall Extension, Manchester. 6.30 p.m.

Friday 18th April Annual General Meeting, details to be announced later. Gas Showrooms, Town Hall Extension, Manchester. 6.30 p.m.

*Continued on page xxxiii*

## MIDLANDS SECTION

*All meetings commence at 7 p.m.*

1951

Wednesday 3rd Oct. H. Unwin, Esq. *Some Methods of Heat and Power Economy in the Dyeworks.* King's Head Hotel, Loughborough

Wednesday 31st Oct. J. S. Ward, Esq., B.Sc. and H. Hampson, Esq. *Some Investigations into the Dyeing of Cellulose Acetate.* Victoria Station Hotel, Nottingham

Wednesday 21st Nov. H. R. Hadfield, Esq., M.Sc. *The Levelling of Water-Soluble Dyes on Nylon.* College of Technology, Leicester

Friday 30th Nov. Ladies' Social Evening King's Head Hotel, Loughborough

Wednesday 12th Dec. *Colloquium.* Short Papers on Practical Problems given by Local Members. Victoria Station Hotel, Nottingham

1952

Friday 18th Jan. Discussion Meeting with the Leicester Textile Society. *The Dyer's Limitations* (With Particular Reference to Mixed Fibres). College of Technology, Leicester

Friday 22nd Feb. Midlands Section Dinner Black Boy Hotel, Nottingham

Wednesday 27th Feb. G. G. Taylor, Esq., B.Sc., A.Inst.P. *The Uses of Microscopy in Textile Dyeing and Finishing* (Joint Meeting with the British Association of Chemists). Midland Hotel, Derby

Wednesday 26th March G. H. Lister, Esq., Ph.D., B.Sc. *The Influence of Dyeing Methods on Fibre Damage.* College of Technology, Leicester

Wednesday 23rd April G. K. Mecklenburgh, Esq., S. Shaw, Esq., and H. W. Peters, Esq. *Some Developments in Setting and Finishing Nylon Textiles* (Preceded at 6.45 p.m. by the Annual General Meeting of the Section). King's Head Hotel, Loughborough

## NORTHERN IRELAND SECTION

*All meetings to be held in Queen's Hotel, Belfast at 7.30 p.m.*

1951

Wednesday 10th Oct. H. Houlker, Esq. (Messrs. L. A. Mitchell, Ltd.) *Drying of Textile Fibres and Materials*

Wednesday 14th Nov. C. P. Tattersfield, Esq. (Courtaulds Ltd.) *Some Dyeing and Finishing Problems with New Fabrics*

Wednesday 12th Dec. R. W. Speke, Esq. (Imperial Chemical Industries Ltd.) *Continuous Dyeing with Vat Dyes*

1952

Wednesday 9th Jan. Dr. G. H. Lister (Sandoz Products Ltd.) *Wool Dyeing*

Wednesday 13th Feb. Discussion Evening

Thursday 6th March R. C. McKinney, Esq. (Lilliput Laundry and Dyeworks Ltd.) *Commercial Laundering in Practice* (Joint Meeting with Textile Institute)

March Annual General Meeting and Dinner (date will be announced later)

THE JOURNAL
OF THE
Society of Dyers and Colourists

Volume 67—Number 9 SEPTEMBER 1951 *Issued Monthly*

# Proceedings of the Society

## The Dyeing of Silk and Silk Mixture Materials

A. Thomson

*Meetings of the London Section held in the Rooms of the Royal Society, Burlington House, Piccadilly, London, on 5th January 1951, Mr. C. C. Wilcock in the chair; and of the Leeds Junior Branch held at the University of Leeds on 30th January 1951, Mr. C. L. Bird in the chair*

The statement: "the art of clothing commenced with the fig leaf and was brought to perfection with the mulberry leaf" is true to-day, in spite of all the excellent man-made fibres now available. Silk is on its way back, as the import of silk from Italy alone in the first quarter of 1950 (50,000 lb.) shows. All fibres, new and old, must be considered as being complementary to one another, each having its particular rôle to play.

In the case of silk there will always be a demand for pure silk stockings and for crêpe de chine, particularly in stripes in the so-called "Macclesfield" style, as these cannot be satisfactorily produced in any other way. Silk has warmth without weight, and its handle, still the aim of the rayon manufacturer, is unrivalled.

About 2600 B.C. a Chinese princess is said to have unravelled a cocoon of silk and realised what a beautiful material could be produced from it. The silk industry developed rapidly, and 3000 years before the Norman conquest the Chinese were cultivating mulberry trees, rearing silkworms, and weaving silken cloth. The secrets of this industry were carefully protected, and death was meted out to anyone found exporting silkworms' eggs or giving information to the foreigner. About the middle of the sixth century, however, two Persian monks managed to smuggle away eggs hidden in hollow canes. These were hatched and the moths reared in Constantinople, so forming the nucleus of the silk industry in the West.

The eggs, only about the size of a pin's head, are fixed to the leaf or a card, as suggested by Pasteur, who was asked to investigate the cause of silkworm disease, which threatened at one time to wipe out the French silk industry. Diseased worms fluoresce differently in ultra-violet radiation, and so may be rapidly picked out and burned.

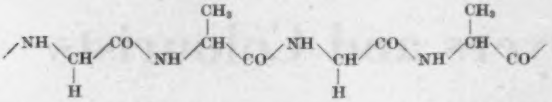
After the incubation period of 10 days the hatched silkworms grow rapidly, shedding their coats four times, and eventually spin their cocoons, using 500–1400 yd. of silk thread. The thread is so light in weight that 1000 cocoons are required to make 4 oz. of silk, and it takes 112 miles of silk to make a pair of silk stockings. Selected cocoons are kept for breeding, and from these the moths emerge some three weeks later. It is interesting to note that neither the worm nor the moth shows any tendency to roam, and this has allowed silk production to become very highly organised.

As the moth breaks out of the cocoon it tears the silk covering; therefore the chrysalides, apart from those wanted for breeding purposes, are killed by treatment with either hot water, dry heat, or superheated steam. The flossy outer coverings are removed, and the cocoons placed in warm water, which softens the silk gum and allows the thread to be unwound. Four or five such threads are collected, and wound off together to form a hank of silk. The waste, consisting of the flossy outer covering and the innermost lining of the cocoons, together with the silk from damaged and pierced cocoons, is degummed, and spun into a multifilament thread known as spun silk.

Each silk thread consists of a central core of fibroin surrounded by an outer covering, amounting to about 25% of the whole, of silk gum or sericin. Two threads are spun simultaneously, and the sericin cements the two together. The silkworm actually has four spinnerets, two supplying fibroin and two sericin.

It is of interest to note that tussah silk consists almost entirely of fibroin. Cultivated silk may be likened to two parallel glass rods, while tussah shows a distinct twist and an irregular cross-section. Astbury[1] has shown that silk is a fully stretched fibre formed by the condensation of $\alpha$-amino acids of general formula $NH_2 \cdot CHR \cdot COOH$ with R appearing on alternate sides every 3·5 A. The side-chain R varies down the chain, but mainly consists of the residues of the two simplest amino acids, glycine and alanine. In the case of wool the chain length is only 3·4 A., but the side-chains are more complex and do not allow the complete

extension possible with silk, which possesses relatively simple side-chains. In the case of glycine $NH_2{\cdot}CH_2{\cdot}COOH$ and alanine $NH_2{\cdot}CH(CH_3){\cdot}COOH$ the residues forming the side-chains are H and $CH_3$ respectively, so that silk may be represented by—



and a single molecule may contain as many as 100 residues each of alanine and glycine.

Both sericin and fibroin are closely related to the true proteins. Sericin resembles gelatin in some of its properties, and contributes largely to the elasticity and strength of the raw silk.

As silk loses 30% in tensile strength and 45% in elasticity when degummed, as many operations as possible are carried out "in the gum". Fibroin is more closely related to the true proteins than to gelatin. Both sericin and fibroin, like other proteins, are colloids possessing both acidic and basic properties; i.e. they are amphoteric.

Silk is a non-conductor of electricity, but has been largely superseded as a covering for electric wires by cellulose acetate and plastics. When silk is used for this purpose it is essential to reduce the ash content to a minimum, and this is best achieved at the isoelectric point of silk, which for many years was considered to be pH 3·7, but recently Howitt [2] has claimed that pH 3·2 is more correct. At this point the combining power of silk is lowest and it is obtained most free from mineral salts. It should then be washed in distilled water till free from acid. When weighted or dyed with mordant dyes it no longer acts as a non-conductor.

To emulate the handle and lustre of silk has long been the aim of rayon manufacturers, and hence most synthetic fibres are artificially dulled. Silk may have its lustre increased by reasonable tin-phosphate loading, but excess loading may impair or even destroy its lustre. It is thought that the weighting causes the silk to swell, so presenting a smoother and more lustrous surface to light. Stretching or stringeing has a similar effect by bringing all the fibres into alignment, and this operation usually finishes any dyeing operation.

Prior to drying, silk is often passed through a bath of organic acid, preferably tartaric, and dried without rinsing, as in this way it acquires a characteristic handle or scroop.

Silk is highly extensible, and can be stretched 14–20% beyond its normal length without breaking. Its tensile strength is extremely high—the breaking *length* of raw silk is 30·8 km.; i.e. in order to break under its own weight a silk thread would require to be nearly 19 miles long.

Silk putrefies only with great difficulty, is rarely attacked by moths, and is only slightly susceptible to mildew. It absorbs moisture readily and has a regain of 11%, though ecru silk will retain as much as 30% of water from a saturated atmosphere.

Silk, unlike wool, does not decompose metallic salts from a boiling bath, but it possesses the power of absorbing metallic hydroxides or basic salts from cold concentrated solutions, and this property is the basis of the mordanting of silk and also of the weighting operations. Raw silk, when degummed, loses 25% of its weight, and the process of weighting originated with the idea of replacing some of this loss. The degree of weighting is reckoned on the final weight of fibroin; e.g. 16 oz. weighting implies that the 12 oz. of fibroin has increased in weight to 16 oz., i.e. to the weight of the silk before degumming. Alternatively, this is referred to as *par*, and the final weighting given as a percentage of par (e.g. 20% over par). Too heavy weighting is to be deprecated, as the resulting material loses the characteristics of silk. Weighting of 20 oz. and 24 oz. is not uncommon in blacks, but for colours a normal weighting is 14–17 oz. Moderately weighted material retains the handle, draping qualities, etc. of silk, and the beauty of the fibre and resistance to wear are improved. In 1948 the International Silk Bureau laid down in detail recommended maximum weightings for silk. For coloured fabrics the weighting varies between 30 and 40% over par and for blacks between 40 and 50%.

Nearly all silk is degummed to-day before use, but as it is more easily and safely handled in the gum it is often woven in this state and degummed afterwards. This applies in particular to silk stockings and to net silk pieces. Similarly, crêpe de chines are woven with the weft consisting of tightly twisted threads of raw silk, alternate threads twisting to the right and to the left respectively (usually referred to as S and Z twists), so that on degumming the tightly twisted threads shrink, forming a crêpe.

Silk may be degummed in a variety of ways, e.g. by the use of water alone under pressure, by alkalis and solutions of alkaline salts, by fermentation and the use of enzymes, by acids, and by soap solution. The actual method to be adopted depends on circumstances. For example, a union of silk and bright acetate rayon could not be degummed by the use of alkali or soap, as the acetate would be either delustred or saponified. If, however, a dull effect on the acetate is required, then the use of soap is desirable. For pure silk the best result is still obtained by the use of a good soap. Olive oil or Marseilles soap is usually recommended, but this is not essential. Any good-quality soap having a low titre, enabling it to be washed out easily, is suitable. Thorough removal is obviously particularly important in the case of soaps likely to oxidise on exposure.

When using soap, a bath containing about 33 lb. of soap per 100 lb. of raw silk is prepared, and the silk passed through the solution in a gentle manner just under the boil (silk stockings are turned inside out and degummed in bags to prevent friction, and pieces are usually degummed on the star frame).

To economise in soap, piece goods may be treated in old and then in new soap baths, while stockings are often degummed with degumming oils consisting e.g. of mixtures of sulphonated castor oil and sodium silicate of high $Na_2O : SiO_2$ ratio.

The latter procedure enables dyeing to be carried out in the same bath, although some dyers still prefer to wash off after degumming and before dyeing.

The constitution and pH of liquor vary with the type of material, and the treatment may last 2–16 hr. or even longer. A pH of 9·2 for the degumming liquor is recommended for minimum damage to the silk fibre, but in practice it is quite usual to degum at pH 10·0 on account of the saving in time. A convenient rapid method of determining the degree of degumming is to use Shirlastain A. The test is best carried out by immersing the material in the stain for a few minutes cold and subsequently rinsing, but a "spotting" technique may be satisfactorily developed, a series of standards being prepared and the degree of degumming estimated with considerable accuracy. As a result of the shortage of soap, many proposals have been put forward for soapless solutions for degumming. These are mainly based on the use of alkali in the presence of a buffer together with some sulphated fatty alcohol or other lime-resistant detergent. Waste silk, Schappe silk, noils, and tussah may be satisfactorily degummed with 5–10% soda ash for 1 hr. near the boil. Great care is required to prevent damage to the fibre by any roughness in treatment or in the apparatus. In spite of this the silk sometimes develops a peculiar fault called *lousiness*. This defect generally shows up after dyeing, particularly in the case of dark shades, as minute apparently undyed specks; under the microscope, however, these are seen to be completely dyed through, the apparent whiteness being due to the reflection of light from numerous surfaces in the same way as a blue crystal of copper sulphate, when crushed, appears white. The trouble is due to the breaking up of the silk fibre into its ultimate filaments, and though it may be inherent in the fibre itself, any rough treatment greatly aggravates the fault. Sizing or oiling of the silk greatly improves its appearance, as the fibres then adhere together.

When only a portion of the gum is removed by using less concentrated solutions at a lower temperature, the silk is referred to as *souple* silk. The remaining gum may be softened by treatment with 3–4% cream of tartar and 1–1·5% sulphuric acid. The yellow colour of some gum silk may be removed by bleaching with nitrous acid or by treatment with aqua regia.

Should silk require to be bleached, hydrogen peroxide and not sulphur dioxide should be used, as the former gives a more permanent result. A liquor is prepared containing 2–3% of 100-vol. hydrogen peroxide (30%) made alkaline with ammonia, sodium pyrophosphate, or sodium silicate. The silk is entered at 100°F., raised to 140, 170, and 200°F., and given time at each temperature. It is then well washed off, and is ready for dyeing white or light colours.

Sodium perborate has been employed for bleaching silk, and the I.G. successfully developed a process using 2–3 g. sodium perborate and 1·5–2 g. Nuva B (a mixture of Igepon T and sodium silicate) per litre, though the handle had a tendency to be rather harsh.

The bleaching of tussah is a much more difficult matter, as each lot may vary from the next because the colouring matter depends on the type of leaves upon which the worm fed. A pure white cannot be obtained, but a reasonable bleach, suitable for use alone or capable of being dyed to quite pale shades, may be obtained by giving a treatment for 2 hr. with 40% of hydrogen peroxide (30%) and 15% of sodium silicate followed by a reduction treatment either for 30 min. at 140°F. with 3% ammonia (sp. gr. 0·880) and 5% sodium hydrosulphite, or with sodium formaldehyde-sulphoxylate at the boil, subsequently washing off, and giving the tussah a repeat treatment with peroxide. The combined oxidation and reduction treatment gives the best tussah bleach but is rather expensive, and often the single peroxide bleach giving a pale fawn colour suffices. Shortly before the war a method using iron as a catalyst was proposed. Iron oxide was precipitated on the fibre, and the material bleached with peroxide; the iron, acting as a catalyst and giving a better bleach, was finally removed with oxalic acid.

The wide range of colours produced and the high standard of fastness obtained by the dyer a century ago with the limited number of natural dyes at his disposal were a tribute to his skill and wide experience. The dyes were usually applied on mordants, and great skill must have been required to reproduce shades. Some of these natural dyewoods are still in use to-day for the dyeing of silk; in particular, logwood blacks are still recognised to be unrivalled on account of their beauty, depth, and filling qualities. Some of the natural and mineral colouring matters, e.g. iron buffs, catechu on copper and chrome, and logwood on iron mordant, dye silk sufficiently fast to withstand the degumming process reasonably well, and were used in the 1914–1918 war and after.

It may be of interest to quote a recipe for dyeing silk a "very fine black" taken from a book [3] published in 1705—

> Take a copper of two tun of water, put in a sack and a half of bark, six pound of Provence wood, six lb. of sumach, boil them 2 hours, then percolate them in a fat, throw away the dregs, and fill up the copper again, and then add 15 lb. beaten galls, 1 lb. agaric, 3 lb. pomgranate shells, 2 lb. of calamus, 3 lb. senna leaves, 2 lb. gentian and two of marjoram; boil them together two hours, then pass the liquor through a sieve into the other dye, and let it digest four days, stirring it often; and then put it into the copper in which you intend to dye. Make a fire under it and when it is hot, put in two pails full of lye, and boil all together very well. This done add 1 lb. antimony, 4 lb. honey, ½ lb. borax, 1 lb. of litharge of silver, ½ lb. litharge of gold, 1 lb. verdigris which beat together and put into the kettle, and when the dye is warm, throw in 30 lb. locksmiths' filings, 20 lb. gum and 20 lb. copperas; let it stand and settle 8 days, stir when occasion demands . . . . . after which you may dye with it, putting in a quart of brandy before you begin.

The last item is particularly interesting—dyeing in those days evidently had its compensations.

With the advent of the synthetic dyes silk came into its own— its beautiful lustre showed off these new colours to their greatest advantage, and for a time fastness became of secondary importance,

whilst brightness and beauty of shade became all-important. This era lasted for quite a while, but has long since passed, and silk may now be dyed with every type of dye available, except perhaps disperse acetate dyes, and even these stain it appreciably.

The actual type of dye used depends upon the degree of processing the material is subsequently to receive and the use to which it is to be put. Each class of dye will, therefore, be dealt with separately, the methods of application and likely uses being indicated.

Owing to the use of soap in both degumming and dyeing baths, it is advisable to use water of zero hardness, preferably obtained by the ion-exchange process, in order to prevent dulling of the silk by the formation of metallic soaps.

### BASIC DYES

Basic dyes are still applied to silk, but in ever decreasing quantities. Pale shades are generally applied from a soap bath, thus ensuring levelness of shade and increased fastness to washing and rubbing. Deeper shades may be obtained by dyeing from a boiled-off liquor (i.e. a liquor containing the silk gum removed in the degumming process) which has been acidified with acetic or sulphuric acid. The silk gum and acid act as retarding and levelling agents. The shades may subsequently be after-treated with 5–10% tannic acid and then, in a fresh bath, with 3–5% tartar emetic to fix the dye and render it faster to both light and washing. It is possible to reduce the number of operations and to simplify matching by applying the basic dye and the tannic acid from one bath provided sufficient mineral acid (sulphuric acid) is present to maintain the tannin–dye lake in solution. The dyeing is subsequently rinsed, developed in tartar emetic, and soaped. Dyeings so obtained are perfectly level, thoroughly penetrated, free from any tendency to rub, and reasonably fast to light considering the type of dye used. It is of interest to note that this process will not give satisfactory results with Methylene Blue, probably owing to complications with the zinc salts generally present in commercial brands of this dye.

Silks dyed with basic dyes, but not aftertreated, may be used for underwear, linings, and ladies' evening gowns. When fixed with antimony really deep shades may be obtained which are fast to washing and milling and reasonably fast to light; they may be used for washing silks, silk stripes in gents' suiting materials which are subsequently to be milled, etc.

### ACID AND DIRECT DYES

As the methods used for the application of direct and neutral-dyeing acid dyes to silk are so similar, and as they are often applied together from the same dyebath, they will be dealt with as one class. This joint class covers a very wide area indeed, the methods of application being similar except for special dyes, which will be mentioned separately.

Normally these dyes may be applied from a soap bath containing Glauber's salt, and here it is necessary to emphasise that only under very strictly controlled conditions should chlorides be used with silk. If they are used at all, chlorides must not be allowed to dry on the silk; complete removal is essential, or the silk will rapidly tender. Both acid and direct dyes dye well when applied in this way, and the two classes may be used in combination. This method is especially suitable for fawns and greys for hosiery and lining shades, but is by no means confined to such shades.

For hosiery the tops and heels can be dyed with suitable direct (Benzanil) dyes, and the silk panel brought to shade with acid dyes, e.g. Fast Silk Yellow S, Sulphonol Red R, and Sulphonol Black B. Such combinations of direct and acid dyes work well together in the same bath in all depths and build up well, yet giving reasonable fastness to light, washing, etc.

Piece dyeing of silk crêpes, satins, etc. is usually carried out on the star frame, although some crêpe de chines, nearly all georgettes, and silk–wool materials may be dyed satisfactorily on the winch. Dyeing by the former method ensures the most careful treatment of the material but has the disadvantage of poor liquor circulation. For this reason and because the dyes with the best neutral-dyeing properties usually possess also the best washing fastness, the neutral-dyeing dyes, both acid and direct, are most generally used for this purpose.

The demands of the high-class tie trade call for entirely different dyes, as the dyeings are expected to possess outstanding fastness to light and not to stain on to white silk, wool, or cotton when steeped together in cold water, so the colours must not bleed off. It is surprising how exacting this latter requirement is, for many dyes will satisfactorily withstand a light soaping test but will fail to pass the water test. The highest-quality ties are frequently woven with silk warp and wool weft to give the necessary resiliency and wearing qualities, and, as dark and light shades often run side by side, this trade can present some very real problems in the way of deep maroons, heavy greens, and bright full royal shades. The former may be obtained with Sulphonol Reds and Black, whilst Alizarine Cyanine Green G forms the basis of the greens, but the bright blues always were, and still are, a problem. The shades of maximum available fastness to light either do not possess the necessary water fastness or the brightness, and it is generally necessary to include blues of the Brilliant Acid Blue type to brighten the shade. In the brown range considerable choice of satisfactory fastness from the Benzanil Supra and Sulphonol ranges is possible. If the silk is weighted the production of deep shades of good fastness becomes still more difficult.

The Sulphonol-type dyes are of outstanding importance to the silk dyer, as within the range are found dyes of good fastness to light, washing, and water, and, moreover, the dyes may be applied from a water-bath with Glauber's salt with or without organic acid, from a boiled-off liquor broken with acid, or even from a soap bath, so that they possess all the desirable qualities together with ease of application.

TABLE I

**Fastness of Benzanil Supra and Benzanil Fast Dyes on Weighted and Unweighted Silk**

(U = Unweighted W = Weighted NS = Not suitable)

| | Light | | Washing | |
|---|---|---|---|---|
| | U | W | U | W |
| BENZANIL SUPRA— | | | | |
| Yellow FF ... | 7–8 | 7–8 | 3 | 2–3 |
| Yellow 7G ... | 5–6 | 3–4 | 2–3 | 2 |
| Yellow GX ... | 7 | 6 | 4 | 3 |
| Yellow 3RLL ... | 7 | 6–7 | 3–4 | 3–4 |
| Yellow 2RLN ... | 6–7 | 4 | 4 | 2–3 |
| Yellow SL ... | 6 | 4 | 3 | 2 |
| Orange AG, AGS | 6–7 | 4–5 | 2–3 | 2–3 |
| Orange ER ... | 5–6 | 4–5 | 3 | 2–3 |
| Orange 2GLL ... | 5–6 | NS | 3 | NS |
| Orange 2RL ... | 6 | 5–6 | 3 | 2–3 |
| Bordeaux BLL | 7 | NS | 4 | NS |
| Red 6BLL ... | 7 | NS | 4 | NS |
| Rubine 2BLL ... | 5–6 | 3–4 | 3 | 3 |
| Scarlet 2G ... | 6 | 5 | 3–4 | 2–3 |
| Brown BRLL ... | 5–6 | 5–6 | 3 | 2 |
| Brown 8RLL ... | 7 | NS | 3–4 | NS |
| Blue 4GL... ... | 5–6 | 3–4 | 3 | 2 |
| Blue 3GLL ... | 7–8 | 4–5 | 3–4 | 2 |
| Blue 5GLL ... | 7–8 | 4–5 | 3–4 | 2 |
| BENZANIL FAST— | | | | |
| Yellow CH ... | 4–5 | 4–5 | 3–4 | 2–3 |
| Yellow G ... | 6 | 4 | 4 | 3 |
| Orange D ... | 6–7 | 4–5 | 3–4 | 2–3 |
| Red F ... ... | 4–5 | 3 | 3 | 2–3 |
| Brown RK ... | 5–6 | 3–4 | 3–4 | 2 |
| Brown 3RL ... | 5 | NS | 3–4 | NS |
| Brown 5RL ... | 5 | NS | 3–4 | NS |
| Brown 6RL ... | 5 | NS | 3–4 | NS |

TABLE II

**Fastness of Neutral-dyeing Acid Dyes on Weighted and Unweighted Silk**

(U = Unweighted W = Weighted)

| | Light | | Washing | |
|---|---|---|---|---|
| | U | W | U | W |
| SULPHONOL— | | | | |
| Red PG ... | 3–4 | 3–4 | 3 | 2–3 |
| Red R ... ... | 3–4 | 3–4 | 3 | 2–3 |
| Brown GS ... | 3–4 | 2 | 4–5 | 2–3 |
| Brown 5R ... | 5 | 4–5 | 4 | 3 |
| Navy G ... | 4–5 | 2–3 | 3 | 2–3 |
| Navy 5RX ... | 3–4 | 2–3 | 3–4 | 3 |
| Black B ... | 6–7 | 2–3 | 3 | 2–3 |
| Black G ... | 6 | 3 | 4 | 3 |

### DIAZOTISED DIRECT DYES

Increased washing fastness may be obtained by the use of dyes which may be diazotised and coupled with e.g. $\beta$-naphthol. Included in this range are Diazodis Blue BRM and RER and Black D giving deep navy blues and black, while Primuline M gives a bright red of excellent washing fastness but of inferior fastness to light. If, however, the Primuline is diazotised and the silk entered into a cold soap solution, which is subsequently raised to the boil, beautiful gold shades are obtained which possess outstanding fastness to light and washing and to the degumming process.

### METALLISED ACID DYES

It is of interest to note that, when the metallised acid dyes are applied to silk, it is unnecessary to use the large amounts of sulphuric acid recommended for the application of these dyes to wool. On silk they may be applied from a dyebath acidified with acetic acid, and the resultant dyeings appear to be almost as fast as those dyed by the normal method.

### MORDANT DYES

The application of mordant dyes to silk offers considerable scope for the silk dyer, as aluminium, chromium, and iron mordants are employed, and all are important for their particular purposes.

#### *Aluminium Mordants*

Basic aluminium sulphate is employed as the mordant and Alizarin Red is the most important dye. Reds comparable with the old Turkey Red are obtained which, even in delicate pink tones, possess outstanding fastness to light and withstand degumming.

The silk is first made alkaline by steeping in warm water containing 3% sodium carbonate ($Na_2CO_3$) on the weight of silk, and squeezed; then steeped in basic aluminium sulphate (18° Tw.) overnight, squeezed, rinsed twice in cold water, and then treated with 5% sodium silicate first at 130°F. and then at the boil. Finally the mordanted silk is soaped at the boil. Alizarin Red IP gives a range of beautiful pinks leading to deep reds. In the case of powder brands, it is useful to dissolve in hot water containing a little ammonia and to precipitate the dye again in the bath in a very fine state of subdivision by the addition of acetic acid.

Dyeing is begun cold, and the dye added in several portions, the temperature being gradually raised to the boil and additions of acetic acid being made simultaneously. The dyeing is then rinsed with hot water, and finally thoroughly soaped at the boil.

In the case of deep shades, brighter and faster dyeings are obtained by aftertreating with 100% aluminium sulphate before soaping in order to fix any loose dye and complete the formation of the aluminium lake.

#### *Chromium Mordant*

Chromium chloride (32° Tw.) may be used for mordanting silk with chromium. The silk is entered into the cold liquor, turned, and steeped overnight. It is then squeezed, thoroughly rinsed in cold water, and, if desired, fixed by treatment with sodium silicate. The addition of sodium sulphate to the chromium chloride solution is said to give improved results.

The use of chromium sulphate, alone or with the addition of caustic soda, of chrome alum, and of chromium acetate for mordanting has been proposed.

Sodium dichromate is unsuitable as a mordant for silk since, although combination with chromic acid occurs, the fibre has no reducing properties

and the chromium is not fixed in the tervalent form. When afterchrome dyes are used on silk, the dichromate develops the shade but does not act as a link between dye and fibre, resulting in loss of fastness compared with similar dyeings on wool.

The use of chrome dyes on silk is not as important as it used to be, since shades of similar fastness may be obtained more easily by other means, but satisfactory results can be obtained by the use of afterchrome (e.g. Durochrome) dyes applied with the addition of Glauber's salt, acetic acid, and sulphuric acid and developed in the same bath with dichromate first at 160°F. and then at the boil.

### *Logwood*

The dyeing of silk with logwood deserves special mention on account of the unrivalled beauty of the shades, which are unobtainable in any other way, the increased weighting obtained, the high standard of fastness of the dyeings, and the wide range of methods of application, enabling it to be applied to weighted as well as unweighted silk.

"Nitrate of iron", also known as "red iron" or "iron liquor" (basic ferric sulphate), and pyrolignite of iron (crude ferrous acetate) are the usual mordants. In the former the silk is steeped for 1 hr. cold in a 52° Tw. standing bath, squeezed, and rinsed thoroughly in cold and then in warm water, thus precipitating in the fibre complex basic ferric compounds. The iron is then fixed or "killed" by a treatment at the boil with 10% soap and 3% soda ash. Thorough "killing" is an essential part of the operation, or unsatisfactory results will be obtained. The iron-mordanted silk should not be allowed to dry, or its affinity for the dye may be altered.

It is possible to dye direct on to this iron mordant from a soap bath using oxidised Hematine Crystals No. 1 and, generally, a little Fustic Extract for shading purposes, starting at 120°F. and slowly raising to 175°F., but it is usual to increase the weighting and improve the shade by including between the mordanting and dyeing processes additional treatments such as dyeing with Prussian Blue and steeping in tannin solution.

The silk is "blued" by treatment with 20% potassium ferrocyanide and 10% hydrochloric acid for 30 min. at 85°F., raising the temperature to 115°F. and then to 120°F. with an addition of a further 10% hydrochloric acid at the latter temperature. Conversion of the ferric hydroxide on the fibre to Prussian Blue increases the weight and improves the shade as well as preventing oxidation of the tannin by the ferric hydroxide during subsequent operations.

Silk is tanned by steeping in a standing bath of Gambier Catechu of 4–6° Tw. for 1 hr. at 120°F., or it may be entered near the boil and turned for 2–4 hr. in a cooling bath. The final temperature should, in any case, be between 100° and 120°F., as both fibre swelling and absorption are greatest over that range. If the silk has been "blued" first the former process should be adopted, as the Prussian Blue is destroyed above 120°F.

To increase the weighting, these processes may be repeated and the silk finally dyed with logwood from a soap bath as before.

Blacks dyed in this way have very good fastness to light (6–7 to 7), perspiration (5), and degumming (5) and, owing to the combination of the tannin and logwood, are more resistant to acids than when the tannin is omitted.

A cold 3–5° Tw. solution of pyrolignite of iron may be used in place of nitrate of iron, the silk being steeped for 30–45 min. On removal, after squeezing, the silk must be allowed to oxidise in air for at least 2 hr. In general, this mordant, giving bluer tones of black, useful for evening wear, is used after the silk has been tanned with Gambier.

It will be obvious from the above that innumerable variations are possible, giving different shades and degrees of weighting.

At one time very heavily weighted silks were obtained by continued repetition of the iron and tannin treatments, but it is usual to-day to obtain approx. 50% of the weighting with tin and phosphate and the remainder with iron and Gambier. It is possible, however, to weight and dye blacks with tin and logwood alone, and this process is often used for degummed yarn and pieces.

Tin–phosphate-weighted silk easily absorbs unoxidised logwood, but it is important to note that the silicate bath must be omitted from the tin-weighting process. A 20–22 oz. black requires two passes through the tin and phosphate baths, and is then further weighted with 100% Logwood Crystals NAD (unoxidised logwood) in a bath made alkaline with soap and 20% soda ash. Enter at 140°F., raise to 195°F. in 90 min., and maintain at that temperature a further 30 min. The colour is then developed by dyeing in a fresh soap bath with 10–20% Hematine Crystals No. 2 together with a little Methylene Blue (preferably zinc-free) and Chrysoidine to correct the reddish tone of the hæmatein–tin lake.

If desired, the absorbed unoxidised Logwood Crystals NAD may be oxidised by treatment, cold, in a bath containing 2% sodium nitrite acidified with acetic or formic acid, the basic dyes used for shading being added to the weighting bath.

The percentages of Logwood Crystals NAD and tin appear to be related, and excess of the former is to be avoided.

Tussah is usually dyed by the tannin–iron method, but no attempt is made to weight the silk other than by formation of the iron–logwood lake.

More detailed recipes are given in various publications [4–7].

## AZOIC DYES

The application of azoic dyes to silk is a comparatively modern development which received considerable attention between the two wars, as these dyes give scarlets, bright reds, deep reds, and browns fast to boiling soap and to bleaching, which are unobtainable in any other way.

In theory the number of possible combinations of ground and base runs into many hundreds, but some have a tendency to rub, some blind the silk as on viscose, others are not fast to bleaching, and some bases and salts couple direct with the silk to give deeply coloured stains which cannot be removed. It follows from this that a limited number of combinations are left which are suitable for use on

silk, and great care must be taken to standardise procedure if reproducible results are to be obtained.

The silk is squeezed after impregnation, and entered, without rinsing, into the cold solution of the developer for 10 min., rinsed cold and then warm, and finally soaped at the boil.

It is inadvisable to mix either grounds or bases, but if this is essential, then in the former case compounds of similar substantivity, and in the latter case of similar coupling energy, should be used.

### SULPHUR DYES

The use of sulphur dyes in practice is confined to greys and blacks. They may be applied to silk satisfactorily in two ways. In the Lodge–Evans process [8], patented in 1914, the dye is dissolved in sodium sulphite to form a solution which is without dyeing properties. This solution is added to the dyebath containing sodium sulphide and ammonium sulphate to form a solution which dyes dark shades (e.g. blacks) quite satisfactorily. Unfortunately hydrogen sulphide is evolved, and as this is objectionable to both men and plant the following method is to be recommended. Add the solution of the dye in sodium sulphite to a dyebath containing, on the weight of silk, 10% ammonia (30%) and 10% hydrosulphite. The solution becomes almost colourless in appearance but dyes silk perfectly level at 130–160°F. from the palest of pale greys to blacks. In the latter case it is necessary to add considerable amounts of common salt to aid exhaustion.

On removing and squeezing the silk, the colour develops immediately, and the dyed yarn can be rinsed and soaped at the boil. The resultant dyeings are reasonably fast to degumming but not to bleaching.

### VAT DYES

The use of vat dyes for the coloration of silk only really developed during the 1920s, though dyeings with indigoid dyes which required the minimum amount of caustic soda in the vat were made during and just before the first world war.

Silk dyes well with the indigoid vat (Benzindone) dyes with one surprising exception— Indigo itself, which merely stains silk. Indigoid-dyed silks possess excellent fastness to washing and can be used for stripes in crêpe de chines if allowance for loss of depth is made.

After dyeing, the silk is wrung out and exposed to air to oxidise, acidified with acetic acid, rinsed, and soaped at the boil.

When the faster anthraquinonoid vat (Benzadone) dyes came to be applied to silk, fears were expressed that the concentration of caustic soda would seriously damage the silk, and attempts were made to apply these dyes from dyebaths containing reduced amounts of alkali, with unsatisfactory results. Additions were then made to the original dyebaths of compounds to decrease the alkali content, or of substances to act as protective agents. Typical of these were, in the one case, *o*-cresol and, in the other, sulphite cellulose liquor, glucose, etc., but often the introduction of another variable only added to the dyer's difficulty without bringing about any substantial improvement in results.

Experience proved that silk could be dyed quite satisfactorily and without material damage to the fibre by dyeing by methods recommended by the dyemakers, though the addition of soap and glue assists penetration and levelness, and in some cases it is possible to lower the temperature a little and complete exhaustion by using additional common salt. By strictly adhering to standard conditions dyeings can be accurately matched and the duration of dyeing reduced to a minimum with beneficial results. The method of finishing is normal—rinse in running cold water, acidify with acetic acid, rinse in warm water, and soap at the boil.

In the case of the developed vat blacks it is advisable to develop with sodium nitrite and sulphuric acid instead of with hypochlorite, thus avoiding the dangerous chloride ion.

Those dyes that accelerate tendering of cellulose fibres bring about tendering of the silk fibroin, so it is advisable to restrict the range of dyes to the non-tendering dyes. Damage to silk may be estimated by determining the fluidity in cupriethylenediamine under controlled conditions [9].

There is no limit to the range of shades available, though deeper shades often require an addition to the dyebath of considerable quantities of Glauber's or common salt. Nigger browns present considerable difficulty, especially when they are required to be scrooped afterwards. Under such conditions the fibre is apparently holding so much dye that it is unable to absorb the organic acid necessary to cause scrooping. This difficulty may generally be overcome by steeping in a 2% solution of a sizing agent and, after squeezing but not rinsing, impregnating in a 2% solution of tartaric acid, squeezing, and drying.

These vat-dyed silks are of particular importance in the manufacture of striped crêpe de chines (Macclesfield silks) and the shades are required to withstand degumming. The Society has published a test [10] for fastness to this process. There should be no material loss in depth or staining on to white silk. This test is stringent enough but is not too severe, as the weft threads in a crêpe de chine are given a high twist, so that when wetted they shrink, and prolonged treatment in the soap solution is required in order completely to remove the silk gum.

The solubilised vat dyes may be applied, like acid dyes, from a bath containing acetic acid. They may be developed with bichrome and sulphuric acid, and as the silk has no affinity for the bichrome, there is no risk of dulling the shade if the correct quantities are used.

### MISCELLANEOUS METHODS

Before considering the dyeing of weighted silk there are a few miscellaneous methods of silk dyeing which may be of interest.

Firstly, the disperse dyes (Serisol, Serinyl, etc.) stain silk quite appreciably, but the resultant dyeings do not compare in shade or fastness with similar dyeings on acetate rayon or nylon. It is therefore quite possible to use these dyes for dyeing the acetate in silk–acetate rayon materials in self or contrasting shades using Sulphonol or Benzanil dyes for the silk.

Interesting results are obtainable by photographically reproducing designs on piece goods. Both positive and negative results are producible from a photographic negative by utilising the power of sunlight to destroy diazo compounds in the one case, or develop leuco vat dye esters in the other.

### SIGHTING COLOURS

It is sometimes necessary in weaving to have the various weft threads tinted to distinguish one from another. Two general types of dyes are employed, firstly acid dyes applied cold without addition, i.e. padded on, and secondly alum lakes of acid dyes. The latter are more easily removed provided the lakes are not fixed by any steaming process, but the former are, in general, more often used. Suitable dyes are given in List I.

LIST I

**Dyes for Sighting**

| | |
|---|---|
| Acid Yellow T | Patent Blue A |
| Quinoline Yellow Y | Naphthol Blue Black |
| Orange II | Acid Green MV |
| Acid Levelling Red 2G | Brilliant Milling Green B |
| Acid Violet 4BNS | |

### WEIGHTED SILK

It is not intended to deal with the weighting of silk in any detail, as methods vary almost as much as methods for dyeing silk black with logwood, but it may be of interest to recall that records exist of weighting being carried out over 300 years ago, it being referred to in a proclamation by Charles I in 1630. At one time sugar was a popular weighting material, but a patent for the use of tin as a mordant for scarlet dyeing was granted in 1748, and there is little doubt that its use as a weighting material developed shortly afterwards.

Tagliani [11] lists thirteen modern methods of weighting silk, including the continuous process of Clavel and Lindenmeyer [12], whereby the silk is made to swell by the action of formic or chloroacetic acid, thus rendering absorption of the weighting materials much easier, and enabling the weighting to be carried out at the rate of one piece per minute.

The process of weighting with tin consists essentially in steeping the silk in cold stannic chloride (54° Tw.), rinsing, and fixing in a warm (140°F.) solution of sodium phosphate (11° Tw.). Each double operation is known as a "pass", and is repeated until the required weighting is obtained. The phosphated silk should be washed, acidified, and hydroextracted before returning to the stannic chloride bath. Unless the silk is to be dyed black with logwood, a final treatment with sodium silicate (4–8° Tw.) at 120°F. completes the weighting process.

Many compounds, such as formates, thiocyanates, thioureas, and hydroxylamine salts, have been recommended as additions to the final bath to stabilise the weighting and prevent tendering.

The presence of the tin in weighted silk narrows down the classes of dyes available for use and restricts the choice of dyes in some classes. Thus sulphur and vat dyes are excluded, and while basic dyes may, in general, be used, there are a number of direct and acid dyes which are definitely unsuitable. In addition dyeings on weighted silk are usually inferior in fastness properties to similar dyeings on unweighted silk. This may be due to the tin acting as a reducing agent or as a catalyst, or to the fact that the silk is more swollen (hence its increased lustre), thus allowing increased ingress and egress of dye and reagent.

Benzanil dyes suitable for weighted silk are given in List II, and the fastnesses of Benzanil Supra dyeings in Table III. Unsuitable dyes are given in List III.

LIST II

**Direct Dyes for Weighted Silk**

BENZANIL—

| | |
|---|---|
| Fast Yellow CH | Fast Red 2BL |
| Fast Orange POS | Fast Bordeaux 2BLN |
| Brown BN | Fast Violet 2BL |
| Supra Brown BRLL | Dark Green BW |
| Fast Red F | Supra Blue 4GL |
| | Black E Extra |

TABLE III

**Fastness of Representative Direct Dyes on Weighted Silk**

| | Light | Washing |
|---|---|---|
| BENZANIL SUPRA— | | |
| Yellow FF ... ... ... | 8 | 2–3 |
| Yellow GX ... ... ... | 6 | 3 |
| Yellow 3RLL ... ... | 6–7 | 3–4 |
| Orange 2RL ... ... ... | 5–6 | 2–3 |
| Brown BRLL ... ... | 5–6 | 2 |

LIST III

**Dyes unsuitable for Weighted Silk**

Acid Dyes

| | |
|---|---|
| Metanil Yellow Y | Victoria Violet 4BS |
| Carmoisine | Naphthol Blue Black |

Direct Dyes

BENZANIL—

| | |
|---|---|
| Supra Orange 2GLL | Supra Brown 3RL |
| Fast Pink BK | Supra Brown 5RL |
| Supra Red 6BLL | Supra Brown 6RL |
| Supra Red Violet R | Supra Brown 8RLL |
| Supra Bordeaux BLL | Burl Black RMW (as black) |

### HALF SILK (SILK–COTTON)

Such materials may be dyed to approximately the same shade with either direct or mixtures of direct and neutral-dyeing acid dyes from a neutral bath containing soap and Glauber's salt. Results are controlled by temperature, liquor ratio, and salt addition. Representative suitable dyes are given in List IV.

LIST IV

**Direct Dyes for Half Silk**

BENZANIL—

| | |
|---|---|
| Fast Yellow CH | Blue RW |
| Fast Orange PR | Supra Brown BRLL |
| Fast Red F | Black E Extra |
| Fast Violet 2BL | |

Two-colour effects on half silk may be obtained in a variety of ways, e.g.—

(1) Dye the silk with acid dyes from an acid bath. Resist the silk by a treatment for 1 hr. just under the boil with—

| | | |
|---|---|---|
| 10% | ... | Resist WL |
| 4% | ... | Formic acid |

Rinse and dye the cotton contrasting shades with Benzanil dyes.

(2) Dye the cotton with direct dyes possessing little or no affinity for silk, the silk being subsequently dyed with acid dyes which do not stain the cotton.

(3) Dye the cotton with direct dyes which possess little or no affinity for the silk but which may be aftertreated in some way, e.g. with formaldehyde, bichrome, Fixanol, etc.; the silk is then dyed, as above, with acid dyes.

Representative Benzanil dyes which dye the cotton much deeper than the silk or leave the latter undyed are given in List V. The same dyes may be used satisfactorily for dyeing the cotton alongside silk treated with Resist WL.

List V

**Direct Dyes colouring Cotton deeper than Silk**

Benzanil—

| | |
|---|---|
| Supra Yellow FF | Supra Blue BL |
| Supra Orange ER | Supra Brown 4RLL |
| Supra Scarlet BL | Black BH |
| Supra Red Violet R | |

List VI gives typical acid dyes which leave the cotton clear when applied either from a Glauber's salt–soap bath or from an acetic acid bath.

List VI

**Acid Dyes leaving Cotton undyed from Neutral or Weakly Acid Baths**

| | |
|---|---|
| Milling Yellow H5G | Milling Brown R |
| Sulphonol Orange G | Brilliant Acid Blue 6B |
| Milling Scarlet 5B | Alizarine Cyanine Green G |

SILK–ACETATE RAYON

These materials may be dyed to self shades by the use of Acetanil dyes or by the use of Benzanil or Sulphonol dyes, applied from a Glauber's salt–soap bath or a weak acid bath, together with selected Serisol dyes which do not stain the silk too heavily. This latter process may be used for the production of contrast effects.

List VII

**Dyes giving Solid Shades on Cellulose Acetate Unions**

Acetanil—

| | |
|---|---|
| Yellow | Green G |
| Orange 3G | Royal Blue R |
| Scarlet G | Navy Blue BN conc. |
| Red B | Black GN conc. |
| Brown BR | |

These materials lend themselves also to clearly defined effects in colour and white. It is not possible satisfactorily to dye the acetate rayon and leave the silk white, as all acetate rayon dyes stain silk strongly, though the stain may be reduced somewhat by treatment with hydrosulphite for azo dyes and by permanganate for anthraquinone dyes. Cleaner and more satisfactory results are obtained by dyeing the silk with direct or acid dyes, either from a soap–Glauber's salt bath or from a bath containing organic acid, which leave the acetate rayon white. Temperatures over 185°F. should be avoided, or the acetate may be affected.

SILK–NYLON

A similar technique to the above may be employed.

GLORIA (WOOL–SILK)

Wool–silk materials are usually dyed with either direct or neutral-dyeing acid dyes. Conditions for obtaining solid shades vary with individual dyes, and results depend on the control of temperature, liquor ratio, and addition of Glauber's salt. Suitable dyes are given in List VIII.

List VIII

**Acid and Direct Dyes for Wool-Silk**

| Acid Dyes | Direct Dyes |
|---|---|
| Milling Yellow 3G | Benzanil— |
| Sulphonol Yellow G | Fast Yellow CH |
| Alizarine Purple RS | Supra Yellow GX |
| Alizarine Pure Blue B | Supra Orange 2GLL |
| Brilliant Acid Blue 6B | Fast Red K |
| Alizarine Cyanine Green G | Fast Violet 2BL |
| Sulphonol Black B | Sky Blue FF |
| | Black E Extra |

Two-colour effects are obtainable by using selected dyes and adjusting temperature and acid concentration or by resisting one of the fibres with Resist WL and topping subsequently with basic dyes; but the result does not justify the work involved, when much more clear-cut and satisfactory results are obtained by weaving into the piece or twisting together wool and dyed and resisted silk threads, the wool being subsequently dyed to shade as required.

The statement made by Tagliani [13] is as true to-day as it was when it was written some seventeen years ago, and forms a fitting conclusion to this paper—

> As it has been down through the ages, it seems certain that materials made wholly from silk, or from silk in conjunction with a small admixture of other fibres, will still continue to be in great demand, in spite of high prices, and even in the future these goods will enjoy great popularity with the ladies, who may possibly think more kindly of the silkworm, for it is—
>
> "A marvellous caterpillar. There are many women who do not like caterpillars. In fact, very few women do. This is unfair. It is really thoughtless ingratitude, as caterpillars have done more for women than any other insects in the world."[9].

* * *

The assistance so freely given by the directors and staff of the Yorkshire Dyeware & Chemical Co. Ltd., and by other dyemakers and silk users who have contributed data and dyeings, is gratefully acknowledged.

Yorkshire Dyeware & Chemical Co. Ltd.
Leeds

**References**

1 Astbury, "Fundamentals of Fibre Structure" (Oxford University Press 1933).
2 Howitt, F. O., "Bibliography of the Technical Literature of Silk" (London: Hutchinson's Scientific & Technical Publications [1946]), p. 52.
3 "Whole Art of Dying" (London 1705).

4 Newsome, O., *Dyer*, **105**, 162 (9th Feb. 1951).
5 Whittaker, C. M., and Wilcock, C. C., "Dyeing with Coal-tar Dyestuffs" (London: Baillière, Tindall & Cox. 5th edition 1949).
6 Ganswindt, "Dyeing Silk, Mixed Silk Fabrics and Artificial Silk" (London: Scott, Greenwood & Son 1921).
7 Howitt, F. O., *op. cit.*
8 Lodge and Evans, *B.P.* 19,473, 23,386 (1914).
9 B. S. Handbook No. 11 (London: British Standards Institution 1949), p. 251.
10 "Second Report of the Fastness Tests Committee" (Bradford: The Society. 2nd edition 1950), p. 12.
11 Tagliani, G., J.S.D.C., Jubilee Issue (1934), p. 186.
12 Clavel and Lindenmeyer, *B.P.* 303,129.
13 Tagliani, G., *loc. cit.*, p. 188.


COMMUNICATION

# Preparation and Properties of Regenerated Cellulose containing Vinyl Polymers

## I—Internal Deposition of Polymers

G. Landells and C. S. Whewell

Using thermal and free-radical polymerisation techniques, conditions have been worked out for the deposition in considerable quantities, inside cellulosic fibres, of vinyl polymers derived from monomers both readily soluble and almost insoluble in the aqueous reaction medium.

### Introduction

Interest in the formation of compounds of high molecular weight inside textile fibres has been largely due to the successful application of urea–formaldehyde resins to cellulosic fabrics, developed in the first place for the production of crease-resistance, but subsequently shown to reduce the swelling of viscose and to confer other valuable properties [1]. It was recognised by the inventors that the important step in this process was penetration into the individual fibres of the urea–formaldehyde condensates of low molecular weight followed by further condensation *in situ*. Evidence that resin is in fact located inside the fibres has been produced by a number of investigators [2–4]. Somewhat similar results have been obtained with condensates of melamine [3], phenol [5], or acetone [3] with formaldehyde.

Until recently, however, judging from the paucity of published information, very little success has been achieved in the formation of addition polymers inside textile fibres. Many addition polymers possess the properties of hardness and water-resistance, which would appear to make their formation inside textile fibres of special interest from both the technical and the purely scientific points of view. The immediate objects of the present research, therefore, were to demonstrate that addition polymers could be successfully formed inside cellulose and to examine the effect of such deposits on the physical properties of treated materials, e.g. water of imbibition and swelling of fibres, and dimensional stability of fabrics.

Speakman and Barr [6], using a vapour-phase technique, first showed that polymerisation inside wool fibres was possible with vinyl monomers, but the treated materials were patchy and the process was not considered to be of immediate technical importance. Illingworth [7] stated in 1942 that, in order to produce resins inside cellulose from water-insoluble monomers, a replacement technique was necessary; that is, the fibres should be first swollen in water, the water then replaced by acetone, and the fibres finally placed in a solution of monomer in acetone containing also the necessary polymerisation catalyst. The method does not appear to have been particularly successful or to have been developed to any extent. A suitable aqueous-phase application became available only with the publication of the Lipson–Speakman [8,9] "anchored-catalyst" technique. This was first worked out on wool fabrics, and is based on the idea of impregnating the fibres with one member of a catalyst combination, namely a ferrous salt, and following this by a solution of monomer and hydrogen peroxide. The initiation of this type of polymerisation has been termed *reduction–activation* or *redox–activation* by Bacon [10], one of the discoverers of the phenomenon. A reduction–activation method on fabric had been employed by Jarrett [11] prior to this discovery of Lipson and Speakman, and is the basis of *B.P.* 572,959, which describes the treatment of textile materials by exposing them to the vapour of monomeric polymerisation compounds containing the group $CH_2{:}C<$ in presence of a reduction–activation system. The mechanism of the ferrous–peroxide catalyst system has been worked out by Evans and co-workers [12–15], and has been shown to involve the production of free radicals according to the following scheme—

$$Fe^{++} + H_2O_2 \rightarrow Fe^{+++} + HO + OH^-$$
$$HO + CH_2{:}CHX \rightarrow HO{\cdot}CH_2{\cdot}CHX-$$
$$HO{\cdot}CH_2{\cdot}CHX- + CH_2{:}CHX- \rightarrow HO{\cdot}CH_2{\cdot}CHX{\cdot}CH_2{\cdot}CHX- \rightarrow \text{Long-chain polymer}$$

The object of the Lipson–Speakman technique is to limit polymerisation to the inside of the fibres as far as possible, and this has been successfully achieved in the production of shrinkproof wool.

It is evident from this brief summary that little work has been published on forming vinyl polymers inside cellulosic fibres, and the present series of papers is an account of an investigation carried out on this topic.

In Part I an account is given of experiments in which suitable methods for depositing various polymers in regenerated cellulose have been worked out, while subsequent papers will deal with detailed studies of the properties of polymer-containing fibres.

## Experimental

An increase in weight following treatment and extraction to remove surface polymer was the main criterion for determining whether polymer had been formed in the filaments. The methods adopted are summarised below, following a description of the materials employed.

### 1. MATERIALS

VISCOSE RAYON MONOFIL (Courtaulds Ltd.), approx. 0·05 cm. in diameter, was chosen for experiments on the determination of increase in weight due to internal polymerisation, and for this purpose was cut into lengths of about 5 cm. A sufficiently large number of specimens was taken to give small bundles each weighing approx. 0·5 g. Untreated specimens were prepared as required, and conditioned at 65% R.H. and 22·2°c., their dry weight being calculated from a moisture content determination on one of the specimens.

VISCOSE RAYON YARN (Courtaulds Ltd., 980 denier, 178 filaments) was employed for the moisture imbibition experiments. Small hanks weighing approx. 0·2 g. (dry weight) were prepared, and tied loosely to prevent unravelling. Some twenty or thirty hanks were usually prepared at the same time, their dry weights being calculated from a moisture content determination on one of the specimens.

MONOMERS used for the impregnation of these materials were as follows—

*Methyl methacrylate* (I.C.I. Ltd.) containing hydroquinone stabiliser, b.p. 100°c., solubility 1·5% at 30°c.*

*Acrylonitrile* (Light & Co. Ltd.), b.p. 78°c., solubility 7·3% at 25°c.

*Styrene* (B.D.H. Ltd.), b.p. 146°c., solubility 0·02% at 30°c., 0·08% at 85°c.*

*Methyl vinyl ketone* (Light & Co. Ltd.), b.p. 78–80°c., soluble in water†.

*Methacrylamide* (I.C.I. Ltd.), white solid, m.p. 109°c., readily soluble in water.

Small quantities of the liquids were distilled immediately before use. This ensured absence of any preformed polymer, and in the case of methyl methacrylate freed the monomer from stabiliser.

### 2. MEASUREMENTS OF WEIGHT INCREASE

In determining increases in weight due to polymer deposition, the specimens, after extraction in toluene or when necessary after thorough rinsing in water, were first air-dried for a short while to remove excess solvent, placed in weighing bottles, and stored over phosphorus pentoxide in a vacuum desiccator at room temperature. Specimens were dried to constant weight, i.e. until changes in weight were less than 0·0005 g. Hanks required at least 7–10 days to reach this equilibrium, but thicker monofil, as is well known [18], required in general about two months' drying at room temperature. In certain cases referred to subsequently, monofils were dried by heating in an oven at 105°c. In the tables of results the amount of polymer deposited is expressed as percentage weight increase calculated on the weight of dry cellulosic material.

* Solubilities of monomers in water by weight, taken from technical literature [16].

† As given by Heilbron and Bunbury [17].

### 3. GENERAL DESCRIPTION OF POLYMERISATION TECHNIQUES

The polymerisation techniques employed may be classified into two general but related types. They were based essentially on the methods described by Lipson and Speakman [8], in which the fibrous material is first impregnated in a solution of a ferrous salt, dried, and then either (i) refluxed at or near the boil for 1–2 hr. in an aqueous solution containing the monomer and hydrogen peroxide, or (ii) heated in the same medium at 25° or 50°c. in an atmosphere of nitrogen. There is little doubt that polymerisation carried out by the first method cannot be regarded as straightforward free-radical polymerisation, for it has been shown that internal polymer deposition may be obtained in absence of ferrous ions. The second method, however, is essentially free-radical polymerisation when carried out under carefully controlled conditions.

Details of the two methods of polymerisation are summarised below.

METHOD (i)— The materials to be treated were placed, after impregnation where necessary with the ferrous catalyst, in a bolt-head flask fitted with a reflux condenser, and aqueous hydrogen peroxide was added followed immediately by the monomer. The contents were shaken and heat was applied immediately. Times taken for the initial production of clouding were recorded from this point. The boiling point was usually reached in about 7–12 min. and treatment was continued for 1–2 hr. under these conditions. After being treated, the materials were rinsed well in distilled water, dried, and then extracted for at least 3 hr. in boiling toluene, the solvent being changed at the end of each hour to remove surface polymer, before determinations of weight increase or other physical properties were made.

METHOD (ii)— The free-radical polymerisations were carried out in vessel *V* (Fig. 1). The specimens to be treated were placed in water contained in *V*, which was then evacuated by closing *A* and attaching *B* to the water pump through a manometer *C* as shown. A pressure of 20–30 mm. was maintained for 2–3 min., when considerable outgassing occurred. A two-way stop-tap enabled the pump

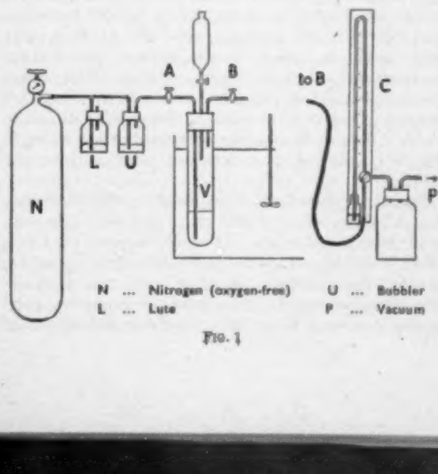



FIG. 1

to be cut out of the system, and nitrogen (oxygen-free) was then allowed to pass into the reaction vessel until the pressure registered on the manometer was restored to atmospheric. This treatment was repeated twice, the whole operation taking about 15 min. After the third outgassing, hydrogen peroxide and monomer were added consecutively, and the mixture was agitated a few seconds by a rapid stream of nitrogen. A slow stream of nitrogen was then allowed to pass through the system during the polymerisation, except in the experiments involving the volatile and highly toxic acrylonitrile, when the reaction vessel was sealed immediately after mixing.

Treated materials were rinsed, dried, and extracted as in Method (i).

## Results and Discussion

### 1. PRELIMINARY EXPERIMENTS— DEGRADATION IN PRESENCE OF VARIOUS AMOUNTS OF CATALYST

It was found that, when the ferrous ammonium sulphate was made up in 0·05 N. sulphuric acid solution for reasons of stability and applied at this concentration, excessive damage to the cellulose occurred on drying at 105°C. for 30 min.; but replacement of the sulphuric acid by 0·1 N. acetic acid reduced this to a minimum, as shown by the results of fluidity determinations given in Table I.

TABLE I

| Treatment of Regenerated Cellulose containing $Fe^{++}$ | Fluidity* ($poise^{-1}$) |
|---|---|
| Untreated ... ... ... ... | 9·3 |
| 0·1 N. Acetic acid, dried at 105°C. ... | 9·7 |
| 1·0 N. Acetic acid, dried at 105°C. ... | 10·1 |

* Determined on 2·0% solutions of cellulose by the standard method of the British Cotton Industry Research Association [19].

Even 1·0 N. acetic acid produced less than one unit rise in fluidity, and damage was regarded as negligible. In all subsequent experiments, therefore, a 0·1% ferrous ammonium sulphate solution in 0·1 N. acetic acid was used to prepare the samples prior to polymerisation.

Specimens are also liable to be damaged by oxidation with hydrogen peroxide, and it was therefore obvious that the lowest possible concentration compatible with effective polymerisation was required. From the results in Table II, which summarise the fluidity of viscose rayon treated for 1 hr. at 95–100°C. with solutions of hydrogen peroxide (liquid : material ratio 40 : 1), both with and without prior impregnation in ferrous ammonium sulphate, it is evident that much greater damage is produced when ferrous ions are present; and this, in view of the results shown in Table I, is clearly not due to acid damage brought about by drying the catalyst solution into the fabrics.

The catalytic effect of traces of iron in producing degradation during oxidation of cellulosic fibres is, of course, well known. It would appear that this effect is explained by the powerful oxidising action of the free radicals produced in the ferrous–peroxide system. The results of the present experiments, however, show that with concentrations of

TABLE II

| Hydrogen Peroxide (%) | pH of Bath (glass electrode) | Fluidity ($poise^{-1}$) Ferrous ions absent | Ferrous ions present |
|---|---|---|---|
| 0·003 | 5·6 | 8·5 | 10·1 |
| 0·03 | 4·7 | 12·8 | 29·1 |
| 0·06 | 4·4 | 16·8 | 34·8 |
| 0·12 | 3·8 | 21·2 | 40·7 |

hydrogen peroxide up to 0·003% little damage is likely to be caused to cellulose in polymerisation treatments involving heating under reflux at or near the boil for one hour. Reactions carried out at lower temperatures would, therefore, almost certainly be free from damaging effects, and might permit the use of even higher concentrations of hydrogen peroxide. In all subsequent experiments concentrations of hydrogen peroxide containing not more than 0·03% have been used in the polymerisations.

### 2. POLYMERISATION IN PRESENCE OF OXYGEN

Polymerisation experiments with various monomers were designed to obtain suitable conditions for the production of internally deposited polymer. Increases in weight of viscose rayon monofil brought about by polymer deposition were determined, and the results are recorded in the tables together with a summary of the reaction conditions employed. The first series of experiments described relates to polymer deposition obtained by refluxing specimens of viscose rayon monofil in monomer solutions at 95–100°C., and to comparisons of the deposit obtained in specimens with and without ferrous catalyst present. The percentages of monomer quoted in the tables are relative to the amount of aqueous solution on a volume/volume basis (with the exception of methacrylamide, the quantity of which is given as weight/volume). The percentages of hydrogen peroxide refer to the actual concentration in the solution. Unless otherwise stated, 0·1% ferrous ammonium sulphate in 0·1 N. acetic acid was used to impregnate the specimens prior to treatment. The ratio of the aqueous phase to cellulose was 100 : 1 in all treatments carried out on viscose monofil. Thus a typical reaction mixture was as follows—

| | |
|---|---|
| Viscose rayon monofil... ... ... ... | 0·5 g. |
| Aqueous hydrogen peroxide (0·0003%) ... | 50·0 c.c. |
| Methyl methacrylate ... ... ... ... | 2·0 c.c. |

A similar method was used for depositing polymer in viscose rayon yarn. Hanks, each weighing approx. 0·2 g. (dry cellulose), were treated in batches of seven. A volume of 100 c.c. of hydrogen peroxide was used for each batch, and the quantity of monomer was maintained at 4%, giving virtually the same system as for monofil treatment but with a slightly lower ratio (70 : 1) of aqueous phase to the yarn.

#### (a) *Methyl Methacrylate*

It was found that polymerisation occurred more rapidly when the monofils contained ferrous ions than when they did not. For example, in Experiment 1 (Table III) with ferrous ions present, clouding occurred in the bath after heating for

10 min., whereas with the corresponding polymerisation in the absence of ferrous ions the time was 15 min. Similar observations were made in experiments employing the same system on hanks, when the corresponding times were 12–14 min. ($Fe^{++}$ present) and 16–18 min. ($Fe^{++}$ absent). In all experiments involving methyl methacrylate no difficulty was encountered in inducing polymerisation, even with hydrogen peroxide concentrations as low as 0·0003%, as judged by the density of the polymer dispersion produced. With this monomer internal polymerisation was usually accompanied by considerable polymerisation in the aqueous phase.

Table III

**Increase in Weight due to Polymer Deposition**

| Sample No. | Methyl Methacrylate (%) | Catalyst Conditions Ferrous Ammonium Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (hr.) | Weight Increase (%) |
|---|---|---|---|---|---|
| 1 | 4·0 | 0·1* | 0·0003 | 2·0 | 15·9 |
| 2 | 4·0 | 0·0 | 0·0003 | 2·0 | 38·1 |
| 3 | 4·0 | 0·1 | 0·0003 | 0·5 | 5·4 |
| 4 | 4·0 | 0·0 | 0·0003 | 0·5 | 28·7 |

* In 0·05 N-$H_2SO_4$.

The results in Table III show that under the conditions described greater increases in weight were actually obtained in absence of the ferrous catalyst. A possible explanation of these results is that desorption of ferrous ions produces greater polymerisation in solution at the expense of internal deposition. It is therefore quite clear that, under these conditions, presence of ferrous ions is not essential for production of polymer internally. As the increases in weight of monofil specimens recorded in Table III were substantial, use of higher concentrations of hydrogen peroxide was not investigated.

### (b) *Acrylonitrile*

This monomer differed from methyl methacrylate in that very little polymerisation occurred if the concentration of hydrogen peroxide was 0·0003%. After treatment for 30 min. under these conditions no weight increases were recorded, and after 1 hr. a small increase in weight (3·1%) was obtained only in the specimen containing ferrous salt. It is known, however, that in the polymerisation of acrylonitrile, if the concentration of hydrogen peroxide is low, there are long induction periods before polymerisation commences [20].

In order to induce internal polymerisation with this monomer a higher concentration of hydrogen peroxide (0·03%) was employed, and comparative treatments were carried out on monofil specimens, both untreated and containing ferrous salt. The treatment was stopped after refluxing for one hour by removing and thoroughly rinsing the specimens. The samples were not extracted because of the known insolubility of the polymer in common solvents. Microscopic examination showed that little, if any, polymer was deposited on the surface of the fibres. The liquid containing no ferrous ions appeared to be more heavily clouded, but the weight increases of the specimens (Table IV) showed, and wet stiffness measurements subsequently confirmed, that greater internal polymerisation had occurred in the presence of the ferrous salt.

Table IV

**Increase in Weight due to Polymer Deposition**

| Sample No. | Acrylonitrile (%) | Catalyst Conditions Ferrous Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (hr.) | Weight Increase (%) |
|---|---|---|---|---|---|
| 9 | 5 | 0·2 | 0·0003 | 1·0 | 0·5 |
| 10 | 5 | 0·2 | 0·03 | 1·0 | 10·3 |
| 11 | 5 | 0·0 | 0·03 | 1·0 | 1·2 |

The method which produced a 10·3% increase in weight on viscose monofil was adopted for treatment of hanks. Individual fibres could be readily separated immediately after the polymerisation, in contrast to the effect produced by methyl methacrylate treatments. This is probably due to the non-film-forming nature of polyacrylonitrile under the conditions examined, and it is considered that the recorded increases in weight (average value 27·7% for the seven hanks referred to above) represents essentially resin formed inside the cellulose structure.

### (c) *Styrene*

Specimens of viscose monofil containing ferrous ions were refluxed in a mixture of 2 c.c. of styrene and 50 c.c. of hydrogen peroxide solution (0·0003%), and a parallel experiment was carried out in which impregnation in the ferrous catalyst had been omitted. No immediate signs of polymerisation were observed in either vessel, and heating was discontinued after 45 min. At the end of this time a slight cloudiness was observed in the bath containing no ferrous ions. After rinsing, extracting with toluene, and drying over phosphorus pentoxide, it was found that the specimen which had been impregnated with ferrous salt showed a weight increase of less than 1·0%, whereas the specimen treated in the absence of ferrous ions had increased in weight by 6·7%. Swelling in cuprammonium hydroxide confirmed this; the specimen which had increased in weight by 6·7% did not dissolve completely, thus giving further evidence of resin penetration, whereas less than 1·0% resin gave no protection against solution.

The effect of increasing the peroxide concentration to 0·03% was therefore examined. Under these conditions clouding appeared fairly rapidly (12 min.) in the vessel containing specimens impregnated in ferrous salt. A slight cloudiness was observed in the second vessel after heating for 19 min. Heating was continued for 1 hr. at approx. 100°c., and it was evident from the opacity of the dispersion that extensive polymerisation had occurred in the reaction vessel with ferrous ions present. The monofil was found to have increased in weight by 21·7%, and in the absence of ferrous ions an increase in weight of 18·0% was obtained (Table V).

The system producing maximum weight increase was chosen for treatment of viscose rayon hanks (1·5 g.). The treated hanks were rinsed in acetone

TABLE V

**Increase in Weight due to Polymer Deposition**

| Sample No. | Styrene (%) | Catalyst Conditions Ferrous Ammonium Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (min.) | Weight Increase (%) |
|---|---|---|---|---|---|
| 12 | 4 | 0·1 | 0·0003 | 45 | <1·0 |
| 13 | 4 | 0·0 | 0·0003 | 45 | 6·7 |
| 14 | 5 | 0·1 | 0·03 | 60 | 21·7 |
| 15 | 5 | 0·0 | 0·03 | 60 | 18·0 |

on removal from the bath and, after drying, were refluxed in boiling toluene for two periods of 30 min. (Refluxing was not continued for the usual 3 hr. because of a tendency of the yarn to shed short lengths of fibre.) Fibres were readily separable from the yarns, and no surface resin was visible microscopically. The average increase in weight for the seven hanks was the remarkably high figure of 123·0%. It is evident, therefore, from the results given above that, in spite of the very low solubility of styrene in water, polystyrene may be deposited inside regenerated cellulose.

### (d) *Methacrylamide*

Attempts to produce polymethacrylamide in the fibres in presence of oxygen at approx. 100°c., by methods already described, were not successful. Hydrogen peroxide concentrations of 0·0003% and 0·03% were employed with solutions of methacrylamide containing, respectively, 4% and 5% of the monomer by weight. No polymer was deposited from solution, and recorded increases in weight were small. The treated monofils dissolved readily in cuprammonium hydroxide.

### (e) *Methyl Vinyl Ketone*

Specimens of monofil, with and without impregnation in ferrous catalyst, were treated in methyl vinyl ketone (5% vol./vol. on aqueous phase, which also contained 0·03% hydrogen peroxide). In presence of ferrous ions clouding started after heating for 7 min., before the solution had reached boiling point; but in absence of ferrous ions clouding started after heating for 14 min. Both treatments caused some gumming together of the individual lengths of monofil by externally deposited resin. According to Morrell [21], methyl vinyl ketone resins are soluble only in ketones and esters. The monofils were, therefore, extracted three times in acetone by refluxing at the boil for periods of 30 min. This extraction removed all visible surface resin, and after drying over phosphorus pentoxide increases in weight were extremely small, being less than 1·0% when ferrous ions were absent and only 1·1% when they were present.

### (f) *Copolymerisation*

It is known that styrene and acrylonitrile are readily polymerised in presence of each other to give copolymers of interesting properties [22]. Experiments on the deposition of such copolymers were, therefore, carried out. For treatment of monofils equimolecular mixtures of the monomers were prepared by mixing 0·01 M. quantities of each, viz. 0·53 g. of acrylonitrile and 1·04 g. of styrene, and these quantities were added to 50 c.c. of the appropriate hydrogen peroxide solution. Owing to different solubilities of the monomers, however, the exact ratio of monomers in solution was not known. All specimens in the present series were impregnated with the ferrous ion catalyst under standard conditions. At low concentrations of peroxide (0·0003%) there appeared to be little if any polymerisation as judged by clouding. Increasing the peroxide concentration to 0·003%, however, caused polymerisation to set in rapidly, and the solution became heavily clouded after heating for 30 min. Similarly heavy clouding was obtained if the hydrogen peroxide concentration was 0·0015% or 0·03%. The corresponding increases in weight of the monofils after refluxing in toluene for 1 hr. are given in Table VI.

TABLE VI

**Increase in Weight due to Copolymerisation**

(Acrylonitrile–Styrene 1 : 1 at 95–100°c.)

| Sample No. | Catalyst Conditions Ferrous Ammonium Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (hr.) | Weight Increase (%) |
|---|---|---|---|---|
| 16 | 0·1 | 0·0003 | 2·0 | 3·8 |
| 17 | 0·1 | 0·0003 | 1·0 | 3·2 |
| 18 | 0·1 | 0·0015 | 1·0 | 26·8 |
| 19 | 0·1 | 0·003 | 1·0 | 76·1 |
| 20 | 0·1 | 0·03 | 1·0 | 56·2 |

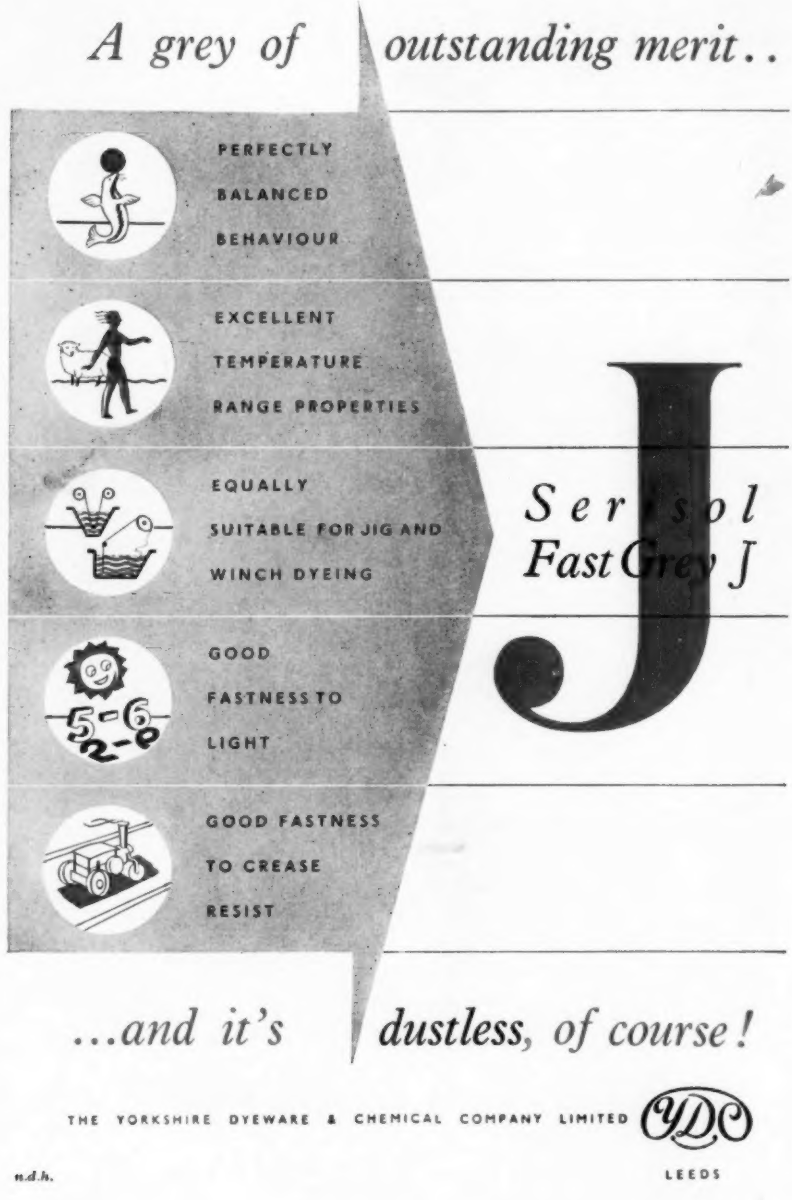
Similar methods employed for the treatment of small hanks of viscose rayon yarn gave average weight increases in presence of 0·03% hydrogen peroxide and 0·0015% hydrogen peroxide of 78% and 35% respectively.

## 3. POLYMERISATION IN AN ATMOSPHERE OF NITROGEN AT 25°C. AND 50°C.

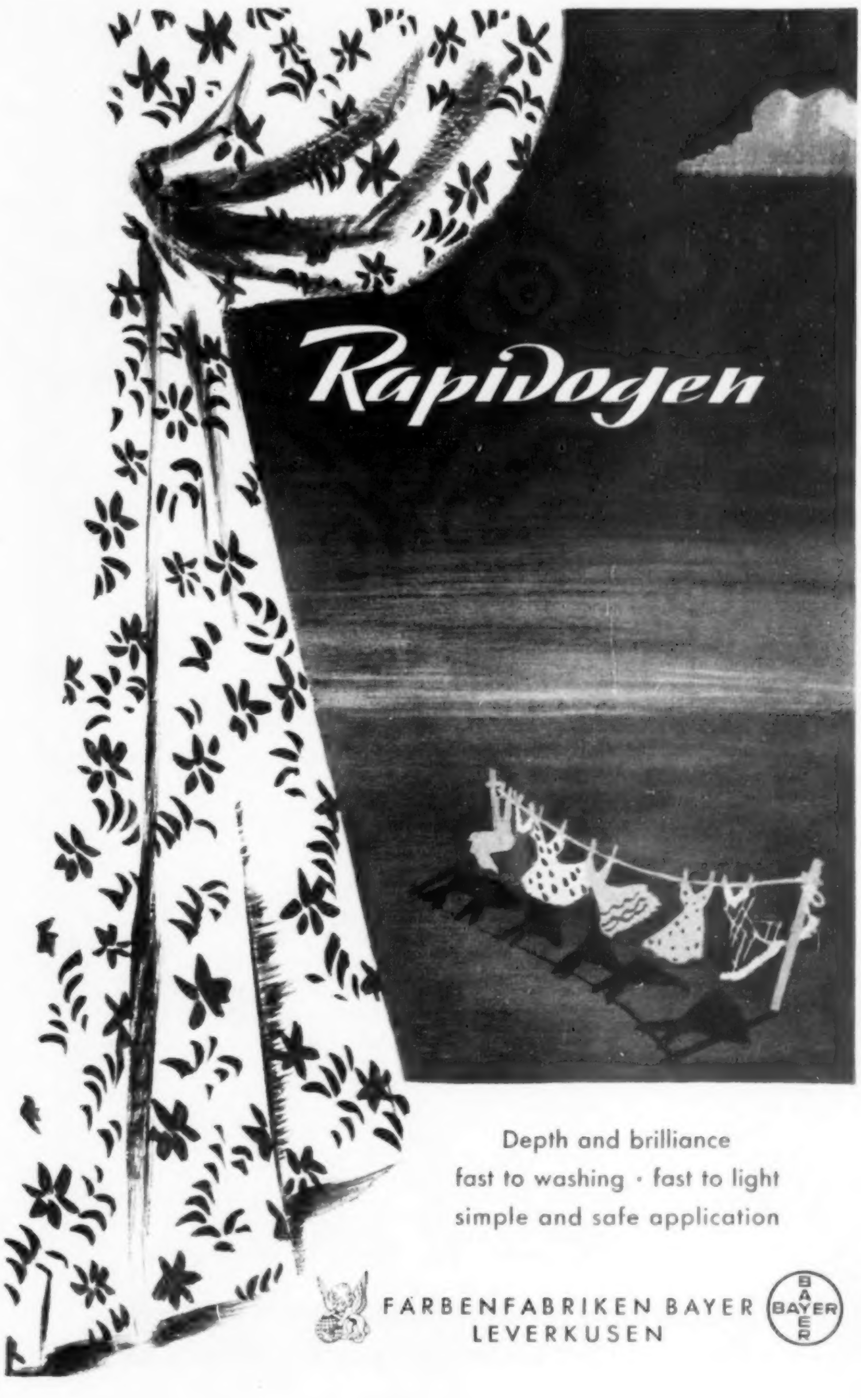
All experiments were carried out in the glass vessel *V* (Fig. 1) by Method (ii) already described. Quantities of materials employed were similar to those given in the foregoing section. Preliminary experiments with methyl methacrylate confirmed that at 25°c. no polymerisation was obtained in absence of ferrous ions. Consequently all subsequent polymerisations at the lower temperatures (25°c. and 50°c.) were carried out only on material containing ferrous catalyst.

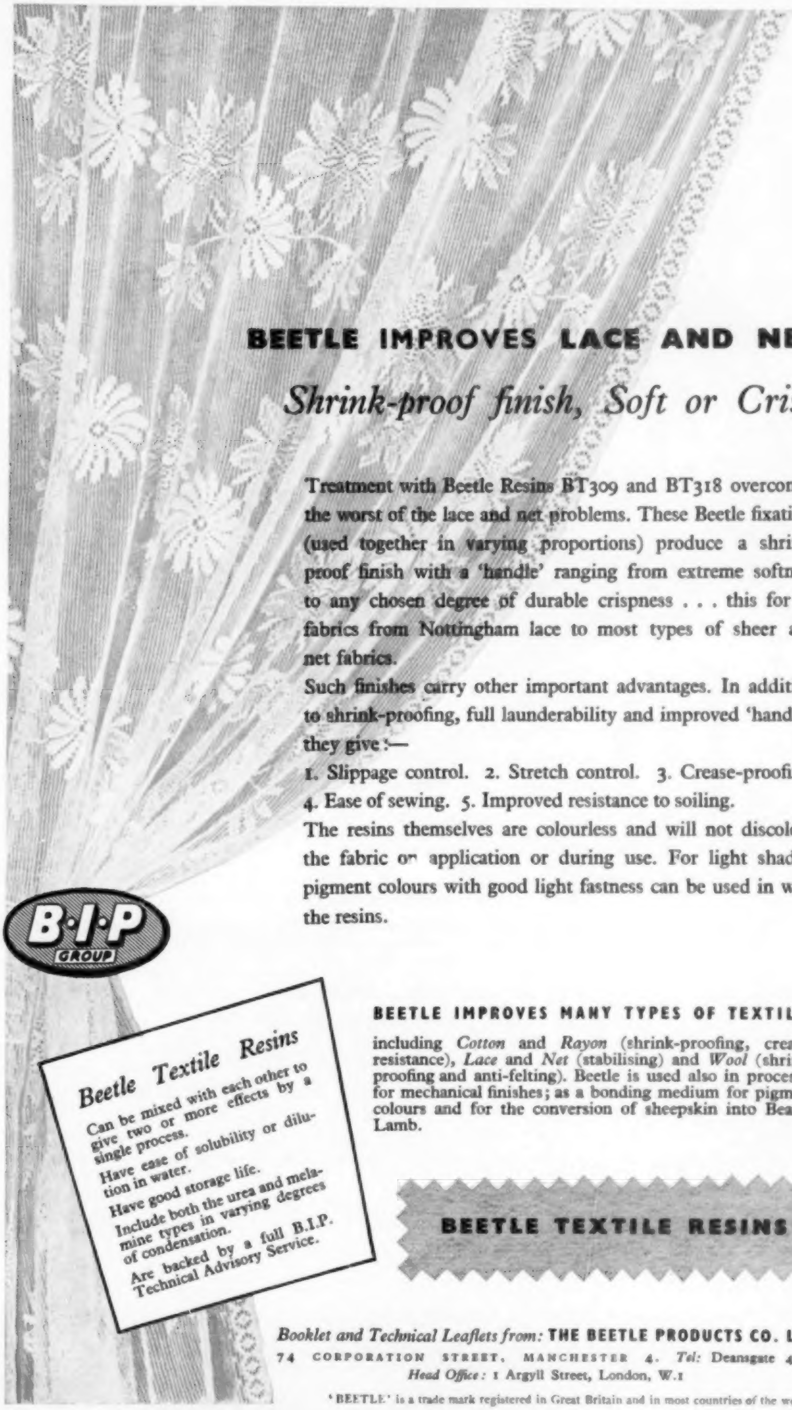
### (a) *Methyl Methacrylate*

In preliminary experiments it was shown that polymerisation could not be initiated at 25°c. when commercial carbon dioxide was used to remove atmospheric oxygen from the system, probably owing to the presence of oxygen as impurity in the carbon dioxide. When commercial nitrogen was used for the same purpose, no signs of polymerisation were observed within 15 min. of mixing, and at this stage nitrogen bubbling was stopped and the apparatus sealed. On examination after 16 hr. it was found that the liquid was only slightly clouded, but a weight increase of 43·7% after extraction showed that internal polymerisation had occurred to a considerable extent. When, however, nitrogen free from oxygen (British Oxygen Co.) was

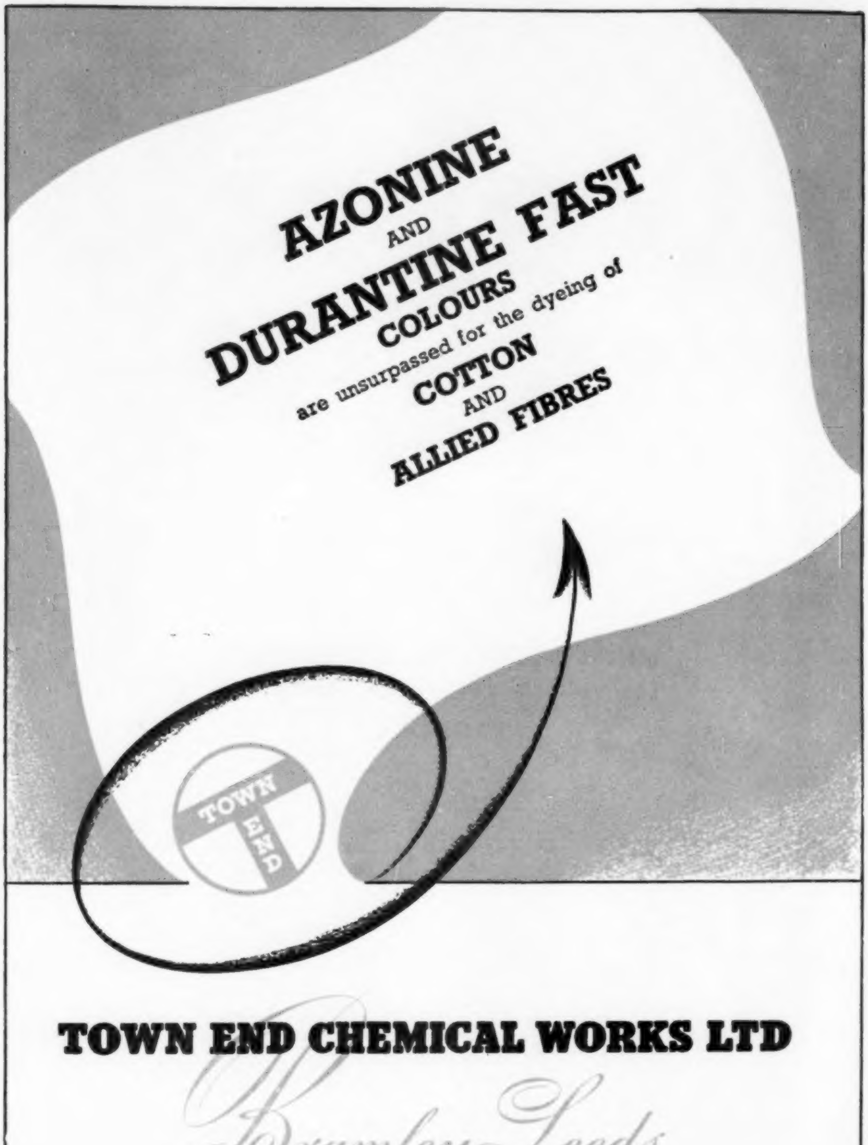

A grey of outstanding merit..
PERFECTLY BALANCED BEHAVIOUR
EXCELLENT TEMPERATURE RANGE PROPERTIES
EQUALLY SUITABLE FOR JIG AND WINCH DYEING
GOOD FASTNESS TO LIGHT
5-6
GOOD FASTNESS TO CREASE RESIST
Ser sol
Fast Grey J
J
...and it's dustless, of course!
THE YORKSHIRE DYEWARE & CHEMICAL COMPANY LIMITED
YDC
LEEDS
n.d.h.


First things first...
No use expecting level dyeing, clear colours or proper finishing without *efficient* chemical auxiliaries. We are specialists in this range, working to an exactitude which sets the standard for the whole Textile trade.
GCL
Textile Auxiliaries for Modern Dyeing and Finishing
PENTRONE (Fatty Alcohol Sulphonates). For Scouring, Cleansing, and Penetrating all classes of textiles. Unaffected by acids, alkalis or hard water.
RESISTONE OP. The perfect mordant for basic colours on all types of materials. Only one hour to mordant cotton, with no fixing bath.
RESISTONE KW. For Union Dyeing. Prevents cotton colours from staining wool. Essential for two-colour effects.
TEXOGENT. Powerful medium boiling-point solvent for Grease, Mineral Oil, Tar, etc. Saves soap in milling and scouring.
TEXOGENT FA. A high boiling-point solvent for use in hot baths and liquors.
RANOTEX A & CW. Softening agent for all classes of fibres.
GLOVERS
LTD
Wortley Low Mills, Leeds 12
Telephone Leeds 38037. Telegrams "Glovers, Wortley, Leeds."


Rapidogen
Depth and brilliance
fast to washing · fast to light
simple and safe application
FARBENFABRIKEN BAYER
LEVERKUSEN
BAYER




Colours you can trust
Your fabrics can be trusted — because you design each one to stand up to its appointed task — no matter how arduous it may be.
Du Pont dyes are designed for their task in the same way — clear beautiful colours which will last as long as the fabric they are used on without fading or bleeding.
Constant research — the finest raw materials — care in manufacture — these are the reasons why you can trust Du Pont dyestuffs.
There is one to suit each of your fabrics.
Diagen Colours — Vat Printing Paste Colours — and other Du Pont dyestuffs and intermediates
send your inquiries for these to the sole U.K. distributors for these products
BROWN & FORTH LTD
118 Chorlton Rd Manchester 15 83-117 Euston Rd London NW1
FINE FABRICS NEED FINE COLOURS
Du Pont Dyestuffs
DU PONT
REG. U.S. PAT. OFF.
BETTER THINGS FOR BETTER LIVING — THROUGH CHEMISTRY


AZONINE
AND
DURANTINE FAST
COLOURS
are unsurpassed for the dyeing of
COTTON
AND
ALLIED FIBRES
TOWN END
TOWN END CHEMICAL WORKS LTD
Bramley Leeds

employed, polymerisation set in almost immediately, clouding being observed within 4 min. of mixing. Treatment for 1 hr. produced an increase of 18·8% in weight. Oxygen-free nitrogen was used, therefore, throughout the remaining experiments.

It was found that successful polymerisation was obtained using 0·0003% hydrogen peroxide. Treatment of hanks of viscose rayon yarn was also carried out using this method, and clouding after 2 min. developed into a deposit of solid white polymer after 15 min. The reaction was allowed to proceed for 2 hr., after which the usual drying and extraction procedures were carried out. An average increase in weight of 30·7% was obtained.

### (b) *Acrylonitrile*

Two treatments on viscose monofil in hydrogen peroxide at a concentration of 0·0003% did not produce much evidence of polymerisation in the aqueous medium. One treatment was stopped after 1 hr. and was found to have produced a weight increase of only 2·1% (Table VII). The same treatment allowed to proceed for 2 hr. gave a weight increase of 25·8%. On hanks, the same reagents (liquor ratio 70 : 1) gave an average increase in weight of only 2·6%. It would appear that at this concentration of hydrogen peroxide long induction periods are encountered, although the polymerisation once started proceeds largely internally. Increasing the hydrogen peroxide concentration to 0·003% and 0·03% and allowing the reactions to proceed overnight produced increases in weight of 55·1% and 59·6%.

TABLE VII

**Increase in Weight due to Polymer Deposition at 25°C.**

| Sample No. | Acrylonitrile (%) | Catalyst Conditions Ferrous Ammonium Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (hr.) | Weight Increase (%) |
|---|---|---|---|---|---|
| 25 | 6 | 0·1 | 0·0003 | 1·0 | 2·1 |
| 26 | 6 | 0·1 | 0·0003 | 2·0 | 25·8 |
| 27 | 4 | 0·1 | 0·003 | 18·5 | 55·1 |
| 28 | 4 | 0·1 | 0·03 | 17·0 | 59·6 |

Similar experiments using the same hydrogen peroxide concentrations at 50°c. again showed (Table VIII) that considerable internal polymerisation could be obtained.

In general, with this monomer, increasing the temperature from 25°c. to 50°c. produced little difference in the amount of polymer deposited, and the lower temperature is therefore satisfactory providing peroxide concentrations are not too low.

TABLE VIII

**Increase in Weight due to Polymer Deposition at 50°C.**

| Sample No. | Acrylonitrile (%) | Catalyst Conditions Ferrous Ammonium Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (hr.) | Weight Increase (%) |
|---|---|---|---|---|---|
| 29 | 4·0 | 0·1 | 0·0003 | 2·0 | 28·8 |
| 30 | 4·0 | 0·1 | 0·003 | 4·5 | 14·9 |
| 31 | 4·0 | 0·1 | 0·03 | 2·0 | 27·8 |

### (c) *Styrene*

Internal polymerisation involving styrene under anaerobic conditions did not in general proceed as smoothly as with acrylonitrile. At 25°c. the weights of monofil samples were virtually unchanged by treatment in presence of 0·0003% and 0·003% hydrogen peroxide, and a weight increase of only 7·6% was obtained in presence of 0·03% hydrogen peroxide (Table IX). As clouding in solution was observed in presence of 0·0003% hydrogen peroxide, the absence of an increase in weight of the specimens is surprising. Similar observations were made, however, during the treatment of hanks. These treatments appear to be examples of the occurrence of external polymerisation without any corresponding internal resin deposition.

TABLE IX

**Increase in Weight due to Polymer Deposition at 25°C.**

| Sample No. | Styrene (%) | Catalyst Conditions Ferrous Ammonium Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (hr.) | Weight Increase (%) |
|---|---|---|---|---|---|
| 32 | 4 | 0·1 | 0·0003 | 2·0 | 0 |
| 33 | 4 | 0·1 | 0·003 | 19·0 | 1·0 |
| 34 | 4 | 0·1 | 0·03 | 20·0 | 7·6 |

Raising the temperature to 50°c. produced a greater degree of internal polymerisation according to the concentration of hydrogen peroxide employed (Table X). The reaction medium at a peroxide concentration of 0·0003% showed first signs of clouding 25 min. after mixing, but this was never very intense. After 5 hr. the specimens had increased in weight by only 3·7%. At a hydrogen peroxide concentration of 0·003% the corresponding increase was 15·3%, and certain bulbous swellings were observed in the specimens. Monofils treated at 0·03% hydrogen peroxide concentration possessed this peculiar characteristic to a greater extent. Most of the short lengths of monofil contained bulbous portions, which at first sight appeared to be "globules" of polystyrene which had merely polymerised in the liquid state on the surface. This appeared quite feasible, as globules of monomer adhered to the monofils on initial shaking. However, extraction in boiling toluene for 4 hr. and soaking for several days at room temperature did not remove these "globules", and manipulation with a mounting needle showed that these bulbous portions were in fact an integral part of the monofil structure.

TABLE X

**Increase in Weight due to Polymer Deposition at 50°C.**

| Sample No. | Styrene (%) | Catalyst Conditions Ferrous Ammonium Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (hr.) | Weight Increase (%) |
|---|---|---|---|---|---|
| 35 | 4 | 0·1 | 0·0003 | 5·0 | 3·7 |
| 36 | 4 | 0·1 | 0·003 | 17·0 | 15·3 |
| 37 | 4 | 0·1 | 0·03 | 19·5 | 25·1 |

### (d) *Methacrylamide*

Three experiments were carried out on viscose rayon monofil at hydrogen peroxide concentrations of 0·0003%, 0·003%, and 0·03% at 25°c. In these treatments the general procedure was modified in one important respect, namely that hydrogen peroxide was added last, as experience from other work [23] has shown that admixture with methacrylamide before introduction of specimens containing ferrous ions tends to inhibit polymerisation. The reaction mixture, therefore, was as follows—

| | |
|---|---|
| Water ... ... ... ... | 47·5 c.c. |
| Methacrylamide ... ... ... | 2 g. |
| Viscose rayon monofil ... ... | 0·5 g. |
| Hydrogen peroxide (0·006%) ... | 2·5 c.c. |

At peroxide concentrations of 0·003% and 0·03% very small increases in weight were recorded (Table XI), and internal polymerisation in appreciable amounts (45·7%) was attained only at the lowest concentration (0·0003%).

TABLE XI

**Increase in Weight due to Polymer Deposition at 25°C.**

| Sample No. | Methacrylamide (%) | Catalyst Conditions Ferrous Ammonium Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (hr.) | Weight Increase (%) |
|---|---|---|---|---|---|
| 38 | 4 | 0·1 | 0·0003 | 16·0 | 45·7 |
| 39 | 4 | 0·1 | 0·003 | 20·0 | 2·7 |
| 40 | 4 | 0·1 | 0·03 | 22·5 | 1·4 |

The conditions giving the highest quantity of internal polymer were used in treatment of viscose rayon hanks, when the slightly lower liquor ratio (70 : 1) was again used. After rinsing to remove surface polymer, and drying, an average increase in weight per hank of 62% was obtained.

### (e) *Copolymerisation*

A limited number of copolymerisation experiments were carried out on viscose rayon monofil to study the effect of altering the peroxide concentration on the formation of polymer at 25°c. and 50°c. The reaction mixture consisted of equimolecular amounts of styrene and acrylonitrile as described on p. 342. Comparatively small increases in weight were obtained at 25°c. over the range of peroxide concentrations examined.

At 50°c. when polymerisation was carried out in 0·03% hydrogen peroxide, the greatest increase in weight (78·5%) recorded for monofil throughout the present work was obtained (Table XII). Features which were particularly marked in the specimen containing the highest quantity of copolymer were bulging at the ends, and distinct zones of penetration, which could be observed clearly at the flat ends of the short lengths of monofil without the aid of a microscope. There was, however, no localised bulging of the monofils as with styrene alone.

TABLE XII

**Increase in Weight due to Copolymerisation**

(Acrylonitrile–Styrene 1 : 1)

| Sample No. | Catalyst Conditions Ferrous Ammonium Sulphate (%) | Catalyst Conditions Hydrogen Peroxide (%) | Time of Treatment (hr.) | Temperature (°c.) | Weight Increase (%) |
|---|---|---|---|---|---|
| 41 | 0·1 | 0·0003 | 18 | 25 | 6·4 |
| 42 | 0·1 | 0·003 | 72 | 25 | 0·0 |
| 43 | 0·1 | 0·03 | 72 | 25 | 11·6 |
| 44 | 0·1 | 0·0003 | 24 | 50 | 0·0 |
| 45 | 0·1 | 0·03 | 18 | 50 | 78·5 |

The work described above provides ample evidence that under suitable conditions vinyl polymers derived both from readily soluble and from almost insoluble monomers can be deposited in regenerated cellulose. As would be expected, the properties of the cellulose are considerably altered by these treatments, and this aspect of the work will be described in Part II of this series.

* * *

We thank the Directors of the Bradford Dyers' Association Ltd. for the award of a Research Fellowship made to one of us, which enabled the present work to be carried out.

TEXTILE CHEMISTRY LABORATORY
DEPARTMENT OF TEXTILE INDUSTRIES
LEEDS UNIVERSITY

(*Received 9th February 1951*)

**References**


1 Marsh, "Introduction to Textile Finishing" (London: Chapman & Hall Ltd. 1947), p. 407.
2 Battye and Alexander, quoted by Marsh, *op. cit.*, p. 410.
3 Landells, *J. Textile Inst.*, **37**, P 317 (1946).
4 Bernegger, *Textil-Rund.*, **3**, 191, 226, 272 (1948).
5 Foulds, Marsh, and Wood, *B.P.* 291,474.
6 Speakman and Barr, *B.P.* 559,787.
7 Illingworth, Post-advanced Course in Textile Chemistry, Manchester College of Technology (1942–43).
8 Lipson and Speakman, *Nature*, **157**, 590 (1946).
9 Lipson and Speakman, *ibid.*, **157**, 736 (1946).
10 Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946).
11 I.C.I. Ltd., Charlton, Jarrett, and Walker, *B.P.* 572,959.
12 Baxendale, Evans, and Park, *Trans. Faraday Soc.*, **42**, 155 (1946).
13 Baxendale, Evans, and Kilham, *ibid.*, **42**, 668 (1946).
14 Baxendale, Bywater, and Evans, *ibid.*, **42**, 675 (1946).
15 Baxendale, Evans, and Kilham, *J. Polymer Science*, **1**, 466 (1946).
16 Blout, Hohenstein, and Mark, "Monomers" (New York: Interscience Publishers Inc.).
17 Heilbron and Bunbury, "Dictionary of Organic Compounds" (London: Eyre & Spottiswoode 1936).
18 Hermans, P. H., "Contributions to the Physics of Cellulose Fibres" (Amsterdam: Elsevier 1946).
19 Clibbens and Geake, *J. Textile Inst.*, **19**, T 77 (1928); Clibbens and Little, *ibid.*, **27**, T 285 (1936).
20 Buck, *Ph.D. Thesis*, University of Leeds (1943).
21 Morrell, "Synthetic Resins and Allied Plastics" (London: Oxford University Press 1947).
22 Mayo, Lewis, and Hulse, *J. Amer. Chem. Soc.*, **67**, 1701 (1945).
23 Fearnley and Speakman, J S.D.C., **66**, 374 (1950).

# Notes

### Meetings of Council and Committees August

Council— 8th
Bye-laws— 1st

---

### Refresher Course for Dyers at Leicester

A Refresher Course for Dyers is announced by the Leicester College of Technology and Commerce in response to a demand from local industry. The Course has been framed to summarise, in straightforward language, present trends in all branches of the dyeing industry. It will be held on six consecutive Saturday mornings from 10 a.m. to noon, from 20th October to 24th November 1951. The venture has the support and advice of the Midlands Section of the Society. A syllabus and enrolment form may be obtained from the College of Technology, the Newarke, Leicester.

# New Books and Publications

### Izbrannye Trudy

**Raboty v Oblasti Organicheskoy Khimii Khimii Krasyashchikh Veshchestv i Teorii Krasheniya**

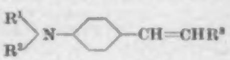
**[Selected Works. Work in Organic Chemistry, the Chemistry of Colouring Matters, and the Theory of Dyeing]**

By A. E. Poray-Koshits. Pp. 466 with biographical sketch and portraits. Moscow and Leningrad: Akademiya Nauk S.S.S.R. 1949. [In Russian.] Price, 40 roubles.

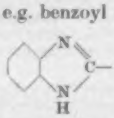
A. E. Poray-Koshits is probably best known to us for his work on the maximum uptake of acid dyes by wool and silk (cf. J.S.D.C., **52**, 19 (Jan. 1936)). He has, however, published a great volume of other work on dyes and dyeing, much of it not readily accessible in this country. The present compilation of his papers was projected in 1947 as a mark of esteem on the part of colleagues and students on the occasion of the author's seventieth birthday. The book was prepared with the co-operation of the author, who has supplied very full notes, mainly concerned with the impact of more modern views on the subject-matter of the earlier papers. Poray-Koshits died shortly before the book was published.

There are twenty-eight papers in all, some of them abridged; only a few can be discussed here. The first is an account, compiled from a group of twelve papers, of benzylation by means of Leucotrope O. Work, published in 1911, on the reactions occurring in the Leucotrope discharge of an indigo ground was followed by a detailed examination of the reactions of Leucotrope O with weakly acidic substances in presence of alkali. It was found that, for benzylation to proceed readily, the dissociation constant of the treated substance must lie within fairly narrow limits, the upper limit being about $10^{-8}$. Thus reaction occurs readily with phenols, hydrogen sulphide, and hydrocyanic and thiocyanic acid, and in most of these cases Leucotrope is superior to benzyl chloride as a benzylating agent. Very often advantage may be taken of the tendency of Leucotrope to benzylate a phenolic group to the exclusion of any carboxyl, alcoholic, or amino group that may be present in the molecule. The reactions of Leucotrope O with anthraquinone in presence of formaldehyde-sulphoxylate were of interest, as they indicated that in these circumstances reduction proceeds beyond the anthrahydroquinone stage, one product of the reaction being 9-benzylanthracene. Dyeings, of excellent wash-fastness but low fastness to light, were produced by padding cotton fabric in an alkaline solution containing Leucotrope O and a *p*-hydroxyazo dye. On ageing, a benzyl ether is formed in the fibre. The same principle was applied to give coloured discharge prints on vat grounds.

In his Ph.D. thesis, presented at Basle in 1905, Poray-Koshits describes work done in Nietzki's laboratory. In the course of this he discovered a new group of basic dyes of the general formula—




where R³ may be e.g. benzoyl or—




When R¹ = R² = H, diazotisation followed by coupling with a suitable component yields interesting dyes, some of which are substantive to vegetable fibres.

Included also is his pioneering work (1911) on the estimation and identification of dyes on the fibre by means of reflection spectra; the theoretical difficulties associated with the method are very clearly recognised. There is also the work already mentioned, in which it is claimed that acid and substantive dyes form definite salts with animal fibres, the saturation limit for strong acids, including dye-acids, being 0·83 mg.-equiv. per gram of wool and 0·20 mg.-equiv. per gram of silk. Other papers relate to tautomerism, colour and constitution, modern resonance theory, the azo coupling reaction, and the chemistry of the three-colour ciné process.

Poray-Koshits has played a great part in the development of the dye and dyeing industries in Russia. Indeed it was he who, in 1908, invented the Russian word for "dye" and established the Russian dye nomenclature. His works reveal him as an experimenter of great ability and wide vision, worthy of a high place amongst workers in the field of dyes and dyeing.

A. E. Stubbs

# Manufacturers' Publications and Pattern Cards

## The Clayton Aniline Co. Ltd.

CHROME FAST DYESTUFFS ON SLUBBING— Seventy-one dyes are shown in this card in three depths of dyeing (except blacks, which are shown in two depths only). Fastness figures for dyeings produced by the after-chrome, on-chrome, and synchromate (single-bath) methods, where applicable, are appended alongside each set of dyeings. In addition to full details for each method of application, the text includes sections on shading and the correction of off-shade dyeings and on auxiliary products suitable for use as dyeing assistants and for producing special finishes.

DYEINGS ON NYLON HOSE— This card contains twenty-three dyeings on nylon hosiery material. Of these, eleven have been produced using individual Cibacet dyes; four, using single Nylocet dyes— mixtures of Cibacet dyes specially suitable for dyeing nylon; the remaining dyeings are fashion shades produced using two- and three-colour mixtures of selected members of both the Cibacet and Nylocet ranges.

FASHION SHADES ON FULL CHROME SUÈDE GOAT— Twenty-four dyeings are illustrated dyed with single and mixtures of Neolan dyes, using formic acid to exhaust the dyebath after 30 min. and dyeing at 50°c.

FASHION SHADES ON RECHROMED ALUM AND SALT SKINS— This card also contains twenty-four dyeings of the same dyes and mixtures of dyes as illustrated in the previous card. The dyeing procedures are also identical, the only difference being that alum-dressed skins have been used and retanned with a basic chromium salt before dyeing.

FASHION SHADES FOR KNITWEAR— This card illustrates twelve dyeings on wool yarn to match the fashion shades No. K 224–235 issued by the British Colour Council for Autumn and Winter 1951.

FASHION SHADES ON WOOL— This card shows thirty-two dyeings on wool piece to match the shades No. B 1213–1244 issued by the British Colour Council for Autumn and Winter 1951. Selected level dyeing acid and Neolan dyes have been used.

FASHION SHADES ON WOOL— Forty dyeings on wool piece matching the shades issued by the Textile Color Card Association of the United States Inc. for Fall 1951 are illustrated in this card.

MODE SHADES FOR LINGERIE ILLUSTRATED ON NYLON TRICOT— This card shows six dyeings on nylon tricot dyed with suitable Cibacet dyes.

FASHION SHADES ON NYLON HOSE— This card contains eight dyeings on locknit hosiery material reproducing the fashion shades D 274–281 issued by the British Colour Council for 1951. Mixtures of Cibacet and Nylocet dyes have been used.

NEOLAN DYES ON ALL-WOOL BLANKETS— This card illustrates twelve single and mixture dyeings on wool blanket material dyed with selected premetallised dyes recommended for this class of trade.

SCREEN PRINTS ON VISCOSE RAYON— This card contains forty-two direct prints on bright viscose rayon piece. Selected acid and direct cotton dyes characterised by brilliance of hue have been used, and urea has been incorporated in the printing paste.

EFFECT OF NON-SHRINK PROCESSES ON CHROME DYES— This table contains the results obtained when medium dyeings of the Chrome Fast dyes applied to wool by the optimum method were subjected to the following five proprietary non-shrink finishing processes— Dylaniz, Epilox, Negafel, Papain, and Woolindras.

CIBANTINE COLOURS ON WOOL— This card contains dyeings on wool yarn of thirty members of the Cibantine range of solubilised vat dyes together with nine mixture dyeings on yarn and five on wool piece. Three dyeing methods are described in the text. In the first, dyeing is carried out using sodium sulphate only as assistant and developing in a bath containing ammonium thiocyanate, potassium dichromate, and sulphuric acid. In the second, Hydrosulphite R Conc. (Ciba) is added to the dyebath, and an acidified solution of sodium nitrite is used for developing. In the third, used with Cibantine Brilliant Green BF only, dyeing is carried out as in Method I but sodium nitrite and acid are used for development. Fastness figures appended indicate that, in general, these dyes exhibit the very high fastness to light and wet treatments even in pale dyeings which is characteristic of this class of dye on wool.

## Imperial Chemical Industries Ltd.

CHLORAZOL, DURAZOL, AND CHLORAZOL DIAZO DYESTUFFS ON COTTON— The complete series of each of these three ranges of direct and aftertreated direct dyes are illustrated in this card on cotton yarn in three depths. The more important fastness figures are given alongside each set of dyeings together with notes on characteristics and uses of each and the dyeing class of the dye according to the classification suggested by the Society.

CHLORAZOL, DURAZOL, AND ICYL DYESTUFFS ON VISCOSE RAYON— This card is very similar to the preceding one, full ranges of direct and aftertreated dyeings being illustrated on bright viscose rayon yarn in three depths except in the case of the diazotised and developed dyes, which are shown in two depths only. The special range of Icyl dyes designed for dyeing viscose rayon having irregular dye affinity are illustrated similarly.

DURAZOL DYESTUFFS ON COTTON— In this card, the complete range of Durazol dyes is illustrated in three depths on bleached cotton limbric. All relevant fastness data are appended alongside the dyeings. Forty-six two- and three-colour mixture dyeings are also included.

BRENTHOL DYESTUFFS ON COTTON— This very large and comprehensive pattern card contains no less than five hundred and ninety azoic dyeings on bleached cotton yarn illustrating in two depths some two hundred and ninety-five combinations from eighteen Brenthols and twenty-five Brentamine Fast Bases or Salts. In addition to figures for the more important fastness assessments, the percentage absorption of the Brenthol and the dyebath concentration of Brenthol, developer, and common salt used for each dyeing are detailed alongside each set of patterns. Methods for preparing the necessary solutions of coupling component and developer and for producing the final dyeing are given in full in the thirty-nine pages of text.

CALEDON AND DURINDONE DYESTUFFS ON COTTON— Ranges of seventy-eight Caledon and nine Durindone dyes are illustrated in this card in three depths of dyeing on bleached cotton yarn. In common with all the more recent pattern cards, relevant fastness figures are appended alongside each set of dyeings and also general remarks on properties and uses of the individual dyes together with notes on any modifications in procedure which should be made to ensure the best result.

ACID DYESTUFFS ON WOOL— In this card, the whole range of acid dyes is illustrated on wool piece in three depths of dyeing (except with navies and blacks, which are shown in two and one depth respectively). They are grouped in four sections— level dyeing dyes, sixty-two members; acid milling dyes, twenty-seven members; Carbolan dyes, twelve members; Ultralan (premetallised) dyes, twelve members. The layout of the card is similar to that of the other cards described above.

DYESTUFFS FOR SISAL— This pattern card contains thirty-six dyeings on thick sisal yarn produced using basic (11), acid (12), and direct cotton (13) dyes. The basic dyes are recommended where brightness of colour is the main consideration; they are applied direct without a mordant. For dyeings having rather better fastness to light, selected acid dyes of good brightness are suggested; and for still higher fastness to light, good penetration, and good fastness to water, direct dyes may be employed.

# Abstracts from British and Foreign Journals and Patents

*(The Titles of Patents are abridged and modified)*

## I—PLANT; MACHINERY; BUILDINGS

PATENTS

**Mixing, Diluting, or Emulsifying Liquids or other Substances.** Société Anonyme Française pour la Séparation, l'Emulsion et le Mélange (Procédés S.E.M.). *B.P.* 654,143.

An efficient and simple form of centrifugal pump for immersing in the mixture to set up intense movement therein is described. C. O. C.

**Wet Spinning of Fibres.** Courtaulds Ltd., H. Barratt, and L. Rose. *B.P.* 653,363.

In the wet spinning of fibres the freshly spun thread is withdrawn upwards from the coagulating bath against the edge of a smooth annular guide rotating at a peripheral speed > the speed of the thread take-up device; by this means the thread rises from the coagulant with practically no disturbance and carries only a thin film of liquid, thus reducing the frictional drag. W. G. C.

**Continuous Treatment and Drying of Running Yarns.** American Viscose Corpn. *B.P.* 654,483.

**Continuous Wet Spinning, Washing, Bleaching, Drying, etc. of Artificial Filaments.** American Viscose Corpn. and R. W. Stanley. *U.S.P.* 2,538,283.

**Thread-advancing Reels.** British Celanese Ltd. *B.P.* 653,346.

**Braiding of Yarn on to Endless Cores or Rings and its Simultaneous Impregnation.** J. M. Marti. *B.P.* 653,526.

**Holding in Contact or Throwing off Co-operating Rollers, Cylinders, etc.** Timsons Ltd., E. A. Timson, and G. R. H. Miles. *B.P.* 654,594.

**Registering Flexible Printing Blocks on Printing Rollers.** A. Navarre. *B.P.* 653,823.

**Laying Fabrics in Folds prior to Feeding into a Stenter or other Machine.** P. Deck. *B.P.* 653,306.

Behind feed rollers driven at a uniform speed there are more slowly driven, cylindrical feed brushes. Part of the periphery of each brush co-operates with a trough whose concave curvature corresponds with the curvature of the brush. Thus folds in the fabric resulting from the difference in speed of the feed rollers and the brushes are brushed through the trough and on to conveyor bands, which carry away the folded fabric from the trough. C. O. C.

**Stop Devices in Web-feeding Mechanism.** Gale & Haycraft Ltd. and B. E. Bradley. *B.P.* 653,710.

**Automatic and Controlled Regulation of the Continuous Application of Solids or Liquids to a Moving Sheet.** British Cotton Industry Research Assocn., E. H. Jones, and S. A. Shorter. *B.P.* 654,178.

The substance to be applied is fed either as neat liquid or in dispersion or solution on to the sheet from a reservoir, to which it is supplied at a rate predetermined by the speed of the sheet and the weight of substance to be applied per unit length of the sheet. Any change in weight of the fluid in the reservoir resulting from a deviation in the actual rate of application of the substance from the prescribed rate is used to alter some property of the fluid in the reservoir so as to correct the deviation. C. O. C.

**High-frequency Dielectric Heating of Sheet Material.** Igranic Electric Co. Ltd. and L. D. Drugmand. *B.P.* 653,794.

**Embossing Thermoplastic Sheet Material.** Boston Woven Hose & Rubber Co. *B.P.* 653,574.

The material is embossed by passing it through a nip, flexible mould plates being placed on one surface of the material to accompany it through the nip. C. O. C.

**Coated Sheet Material.** American Viscose Corpn. and C. S. Francis, Jr. *U.S.P.* 2,537,126.

Apparatus is described in which a fibrous base is given a coating which has a permanently depressed design in it, the body of the base material being relatively free from coating material. C. O. C.

**Compressive Shrinking and Finishing Blanket.** Albany Felt Co. and Z. J. Chagnon. *U.S.P.* 2,536,974.

Incorporation of 5–70% of nylon into the weft yarn results in blankets of appreciably longer life. C. O. C.

**Applying Legends and other Markings to Fabrics.** Milford-Astor Ltd. and W. E. Imago. *B.P.* 653,665.

**Screen Printing Frames.** M. De Pasquale and B. Kushner. *U.S.P.* 2,537,306.

A frame is described which, while permitting the stencil to be readily inserted and tensioned, prevents wrinkling and puckering of the screen by eliminating warping of the frame. C. O. C.

**Laundry Ironing Machines.** N. V. Machinefabriek Reinveld. *B.P.* 654,010.

**Drying Hides, Skins, etc. by Infra-red Lamps.** F. S. Bryant Ltd., R. S. Bryant, and G. E. Buckby. *B.P.* 654,800.

**Resin-treatment of Endless Felts.** Orr Felt & Blanket Co. (X, p. 356.)

## II—WATER AND EFFLUENTS

PATENT

**Electrical Purification of Water.** F. Pavelka. *B.P.* 653,350.

Apparatus for the electro-osmotic purification of water containing dissolved salts comprises an outer electrode serving as the container, an inner electrode, and between them at least one cylindrical diaphragm; the electrodes and diaphragm are arranged concentrically, and the outer electrode is preferably square with the pipe lines disposed in the corner spaces. J. W. B.

## III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

**Fatty Alcohols from Wool Wax Unsaponifiables by Urea-complex Formation.** E. von Rudloff. *Chem. and Ind.*, 338–339 (28th April 1951).

Fatty alcohols may be separated from the other constituents of wool wax unsaponifiables by forming complexes with urea. The best method of isolation consists in refluxing the unsaponifiables (100 g.) with urea (55 g.) in ethanol (750 ml.) and cooling. The precipitated complex is filtered off, and a second crop obtained by adding 40 g. urea to the filtrate, whilst a third crop results from reducing the volume of the second filtrate. After recrystallising from ethanol, the complex is decomposed in a mixture of water and ether, yielding mixed alcohols (21 g.) consisting of monohydric alcohols with a small amount of dihydric alcohols. The former could not be resolved into single components by either column chromatography or fractional crystallisation. W. K. R.

**Colloidal Structure of Spinning Oils and Greases.** E. H. Kadmer. *Melliand Textilber.*, 32, 377–383 (May 1951).

PATENTS

**Detergents.** California Research Corpn. *B.P.* 653,702.

The detergent properties of non-cationic surface-active organic detergents are greatly increased by addition of a small quantity of a water-soluble salt of celluronic acid, i.e. the product obtained by oxidising only the primary $CH_2OH$ groups of anhydroglucose units in the cellulose molecule to convert them to carboxyl groups. C. O. C.

**Germicidal Detergents.** Lever Brothers & Unilever Ltd., B. J. F. Hudson, and A. D. Scott. *B.P.* 654,139.

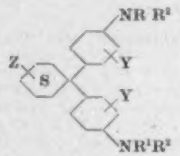
Halogenated *oo'*-dihydroxydiphenyl ethers, unlike many other highly efficient germicides, retain an effective germicidal action when incorporated in soap in small quantities. C. O. C.

**Water-soluble Cellulose Ethers.** British Celanese Ltd., J. Downing, and J. G. N. Drewitt. *B.P.* 654,014.

Presence of a small proportion of carboxymethoxyl groups in methyl cellulose raises its coagulation temperature so that it remains soluble in water up to 100°C. C. O. C.

**Gas-fading Inhibition with *pp'*-Diaminodiphenyl-*cyclo*hexane Compounds.** General Aniline & Film Corpn. and J. J. Hayden. *U.S.P.* 2,536,640.

Compounds of formula—




(S = a *cyclo*hexane ring; Z = H or $CH_3$; R¹ and R² = H or Alk; Y = H, Hal, Alk, or alkoxy) are highly effective gas-fading inhibitors. They are insoluble but readily dispersible, have affinity for organic derivatives of cellulose, and are fast to washing and dry cleaning. C. O. C.

**Linear Polyamide Resins of High Molecular Weight.** Monsanto Chemical Co., D. T. Mowry, and E. L. Ringwald. *U.S.P.* 2,537,689.

Polyamides of structure $[CO{\cdot}R{\cdot}NX{\cdot}R{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}NH]_n$ (R = bivalent hydrocarbon radical; $n$ = a whole number; X = H, Alk, Ar, aralkyl, or *cyclo*alkyl of $<$ 19C) are obtained by condensing formaldehyde with aminodinitriles having the amino group in the straight chain between the nitrile radicals. They are particularly useful for increasing the strength of paper or as animalising, sizing, or finishing agents for textiles. In addition they may be used for increasing and controlling the viscosity of aqueous solutions and as dispersing and stabilising agents for aqueous emulsions. C. O. C.

**Hydrophilic Aminotriazine–Aldehyde Resins.** British Industrial Plastics Ltd. and W. M. Thomas. *B.P.* 654,305.

Water-soluble neutral or alkaline, hydrophilic resins are obtained by treating hydrophilic aminotriazine–aldehyde resins with an alkali-metal sulphite or hydrosulphite under alkaline conditions. They may be used for increasing the wet strength of paper, rendering cellulosic fabrics crease-resistant, bleaching leather, and as adhesives. C. O. C.

**Guanylmelamines and Acid Salts thereof—Flame-proofing Agents and Intermediates for Dyes and Textile Agents.** American Cyanamid Co. *B.P.* 653,520.

Guanylmelamine hydrohalides are obtained by heating dicyandiamide and a hydrogen halide at $>$ 40°C. in absence of water. They are useful as flameproofing agents and as intermediates for dyes and auxiliary agents. C. O. C.

**Oil-in-water Type of Emulsion for Simultaneously Colouring and Flameproofing Fabrics.** American Cyanamid Co. and F. Fordemwalt. *U.S.P.* 2,536,978.

A film-forming, colourless, fire-resistant, water-insoluble, non-volatile organic compound containing 2–12% of combined Cl and liberating HCl on heating is made into a smooth paste with 5–30% of a colourless fire-retarding pigment, e.g. antimony oxide, and just enough of a hydrocarbon solvent to impart fluidity. A second paste is formed by blending a colouring pigment, e.g. iron oxide, with a solvent solution of 0·5–10·0% of a drying-oil-modified alkyd resin and/or a hydrocarbon-soluble amide–aldehyde resin. These pastes are then separately dispersed into an alkaline aqueous solution containing 0·1–10·0% of a hydrophilic colloid and 0·25–4·0% of a water-soluble soap of a higher fatty acid. The amounts given are in all cases weight percentages of the final emulsion. C. O. C.

**Flame- and Mildew-resistant Colouring Compositions for Cellulose Fibres.** American Cyanamid Co. and R. D. Vartanian. *U.S.P.* 2,536,988.

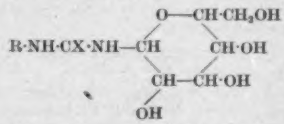
A film-forming, colourless, water-insoluble, non-volatile organic compound containing 2–12% of combined chlorine and yielding HCl when heated (5–30% by weight on the final composition), a colourless fire-retardant pigment (6–15%), and enough organic solvent to impart fluidity are formed into a paste. Similarly a colouring pigment is pasted with an uncured, heat-convertible drying-oil-modified alkyd resin and/or an organic solvent soluble amide–aldehyde resin (0·5–10%) made into a concentrated solution in an organic solvent. These two pastes and a halogenated phenol (0·3–2%) dissolved in a water-soluble sulphonated oil are stirred separately into an alkaline aqueous solution of a hydrophilic colloid (0·1–10%), a water-soluble soap of a fatty acid (0·25–4%), and a water-soluble phosphate afterglow preventative (1–5%). Materials treated with this composition have a soft, flexible handle and withstand extended weathering without excessive loss of either colour or flame or mildew resistance. C. O. C.

**1-*p*-Chlorophenyl-2-nitro-1-tolylpropane — Mothproofing Agent.** Purdue Research Foundation, H. B. Hass, and M. B. Neher. *U.S.P.* 2,538,687.

1 - *p* - Chlorophenyl - 2 - nitro - 1 - tolylpropane possesses marked insecticidal properties and is a highly effective mothproofing agent; e.g. mohair cloth impregnated with a 0·062% solution of the agent in acetone was completely immune to the attacks of black carpet beetle larvæ. C. O. C.

**Nitrogenous Derivatives of Hexoses for rendering Cellulose Textiles Crease- and Shrink-resistant and Paper Moisture- and Water-resistant.** O. J. Meijer's Dextrinefabrieken N.V. *B.P.* 653,775.

Compounds of formula—




(R = H, Alk, Ar, or aralkyl) react with cellulose in presence of aldehydes. They are obtained by treating hexoses in presence of a dehydrating agent with a compound of formula $R{\cdot}NH{\cdot}CX{\cdot}NH_2$ (X = O, S, or :NH) or with melamines. C. O. C.

**Polymers and Copolymers—Coating Compositions.** Monsanto Chemical Co. and G. R. Barrett.

*U.S.P.* 2,537,015.

Compounds of formula $Ar{\cdot}CH{:}CR{\cdot}NO_2$ (R = H or a univalent hydrocarbon radical) are catalysts for the polymerisation of unsaturated compounds.

*U.S.P.* 2,537,016.

Copolymers of compounds of formula $R{\cdot}CH{:}CH_2$ (R = subst. or unsubst. phenyl) with an alkyl acrylate and an alkyl half-ester of an ethylene-$\alpha\beta$-dicarboxylic acid are useful in paper, textile, and leather finishing, particularly in coating compositions. They can be vulcanised or cured in presence of compounds showing polyreactivity for carboxyl groups, e.g. polyethyleneamines, polyglycols, polyvinyl alcohol, and melamine–formaldehyde resins.

*U.S.P.* 2,537,017.

Coating compositions especially suitable for rug backings and for lightweight fabrics contain as the film-forming materials (1) polyvinylbutyral and (2) a copolymer of a secondary alkyl half-ester of an ethylene-$\alpha\beta$-dicarboxylic acid with a compound of formula $R{\cdot}C_6H_4{\cdot}CH{:}CH_2$ (R = H, $CH_3$, or Hal).

*U.S.P.* 2,537,018.

Quick-drying coating compositions which yield hard flexible films possessing good adhesion to non-flexible surfaces contain as the film-forming component a copolymer of a secondary alkyl half-ester of an ethylene-$\alpha\beta$-dicarboxylic acid (Alk of 4–12 C) with a compound of formula $R{\cdot}CH{:}CH_2$ (R = subst. or unsubst. phenyl).

*U.S.P.* 2,537,019.

An inexpensive coating composition for application to flexible or non-flexible materials to yield a hard, flexible, solvent-resistant coating contains as the film-forming ingredients (1) a copolymer as described in *U.S.P.* 2,537,018 (above) and (2) an amino–aldehyde thermosetting resin.

*U.S.P.* 2,537,020.

The above types of polymers are obtained by heating a mixture of a polymerisable vinyl compound, e.g. styrene, and an ethylene-$\alpha\beta$-dicarboxylic anhydride, e.g. maleic anhydride, in presence of an alkyl half-ester of an ethylene-$\alpha\beta$-dicarboxylic acid (Alk of 1–3 C), the latter being added before or during the heating. Once initiated, the polymerisation reaction is highly exothermic, and the mass must be cooled to keep the reaction under control.

C. O. C.

**Water-repellent Finish.** Monsanto Chemical Co. and J. C. Harris. *U.S.P.* 2,537,667.

Melamine- and urea-formaldehyde condensates and alkyl ethers of methylolamine and dimethylolurea can be condensed in neutral aqueous solution or dispersion in presence of a neutral compound of formula—

Alk·CO·NH·$CH_2$·NH·CO·Alk

(Alk of 11–27 C). The condensation may be carried out not only under neutral conditions but also in presence of substances of pH > 7. The condensates formed under alkaline conditions are used for giving a water-repellent finish to textiles which are liable to be tendered by acids. A suitable composition for imparting a water-repellent finish to cotton consists of a dispersion of pH 9–10 and particle size 0·5–10·0 $\mu$. of *NN'*-distearoyldiaminomethane (3·5–15·0% by weight), a hydrocarbon-soluble resinous dibutyl ether of tetramethylolmelamine (8–24), oleic acid (3·5–8), 28% ammonia (4–8), and water (to make up to 100). C. O. C.

**Tannic Acid from Sumac Leaf.** G. Carrara. *U.S.P.* 2,537,510.

Light-coloured tannin of low sp. gr. is obtained by percolating water at not > 50°c. through pulverised sumac leaves until 50–55% of the tannin content of the leaves has been removed as an aqueous solution. This is then concentrated to 10–12° Bé., cooled to 0°c., concentrated to 28–30° Bé., and finally extracted with 1·2 parts of ethyl acetate to 1 part of aqueous solution. C. O. C.

# IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

**Catalytic Reduction of the Aromatic Nitro Group in Aqueous Solution.** F. Allisson, J. L. Comte, and H. E. Fierz-David. *Helv. Chim. Acta*, **34**, 818–822 (May 1951).

Raney nickel is suitable for the catalytic reduction of aromatic nitro compounds in aqueous solution, but in comparison the new nickel formate–paraffin catalyst (preparation described) offers several advantages over it, viz. stability, insensitivity to air and chlorides, and wider applicability. In the catalytic reduction of nitro compounds, the aqueous solutions are buffered at pH 5–6, the hydrogen intake is generally quantitative, and the expected yield is almost theoretical. The examples described are the reductions of sodium nitrobenzenesulphonic acid, *o*-nitrobenzoic acid, and *p*-nitrophenol, and the preparations of Koch's and Cleve's acids from naphthalene and sodium naphthalene-$\beta$-sulphonate respectively. H. H. H.

**Hydrolysis of 2:6:8-Naphtholdisulphonic Acid during the Sulphonation of $\beta$-Naphthol.** I. I. Vorontsov. *J. Appl. Chem.* (*U.S.S.R.*), **24**, 332–336 (March 1951).

The principle of producing 2:6-naphtholsulphonic acid by sulphonating $\beta$-naphthol under conditions that favour the hydrolysis of an 8-sulpho group (cf. J.S.D.C., **66**, 66 (Jan. 1950)) is now extended to the problem of disulphonating $\beta$-naphthol to give a maximum yield of the valuable 2:3:6-acid to the exclusion of the 2:6:8-acid. Following a procedure analogous to that described previously, it was established that even under the sulphonation conditions most favourable for the hydrolysis of an 8-sulpho group (in 91% $H_2SO_4$, 2·67 moles per mole of $\beta$-naphthol; 100–105°c.), 20–25% of the 2:6:8-isomer was formed. Much the same result was obtained when the $\beta$-naphthol was first sulphonated with oleum to give mainly the 2:6:8-acid, and the mixture then diluted to establish the conditions for hydrolysis. A. E. S.

**Action of Methylsuccinic Anhydride on certain Xylenols, and Synthesis of some Trimethylnaphthols.** W. Cocker, A. K. Fateen, and C. Lipman. *J.C.S.*, 926–929 (April 1951).

The condensation of methylsuccinic anhydride with the methyl ethers of *o*-3-, *o*-4-, *m*-4-, and *p*-xylenol has been studied in nitrobenzene, benzene, and carbon disulphide, and the proportions of the respective derivatives of the $\alpha$- or $\beta$-methylpropionic acids formed are expressed in tabular form. Each keto acid was reduced to the corresponding butyric acid, which was cyclised to the tetralone, from which the corresponding naphthol was obtained by conventional methods; 3:4:6-trimethyl-1-, 3:4:7-trimethyl-2-, 2:4:7-trimethyl-1-, and 1:4:7-trimethyl-2-naphthols are described. H. H. H.

**Dyes.** E. A. Sack. *Teintex*, **16**, 233–255 (May 1951).

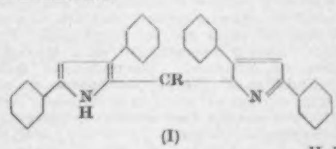
A historical review of the principal discoveries of dyes from Mauveine to present-day products. B. K.

**Colour of Organic Compounds. I—A General Colour Rule.** E. B. Knott. *J.C.S.*, 1024–1028 (April 1951).

Förster's colour rule (*Z. Elektrochem.*, **45**, 548 (1939)), which can, by definition, be applied only to ionic dyes, and considers that $\lambda_{max}$ of the dye will increase with a decreasing tendency of the chain of atoms (chromophores) lying between the auxochromes to take up the characteristic charge, is now modified to cover non-ionic as well as ionic dyes; viz. $\lambda_{max}$ will increase as the contributions by any of the interauxochromic, ionic excited structures decrease. Since the contributions by the various structures depend largely on their relative energies, it follows that $\lambda_{max}$ will be increased by raising the energy of any one interauxochromic, ionic, excited structure. An empirical method is given to allow the rule to be applied by organic chemists, and tables of examples of various dye types are included to illustrate its working. It is also shown that this rule can be restated in terms consistent with the conclusions of Kuhn (*J. Chem. Physics*, **17**, 1198 (1949)) from the electron-gas model; viz. that for any particular length of conjugation the more uniform the potential field of the system the larger will be the calculated value of $\lambda_{max}$. H. H. H.

**Colour of Organic Compounds. II — Colour Phenomena of Bis-2-(3:5-diphenylpyrrole)-methins.** R. A. Jeffreys and E. B. Knott. *J.C.S.*, 1028–1030 (April 1951).

The abnormal colour change shown on salt formation by solutions of bis-2-(3:5-diphenylpyrrole)phenylmethin (I: R = $C_6H_5$), viz. from red to green on acidification, is very interesting in view of the relative insensitivity of the parent dye (I: R = H) to change in pH, solutions of the latter dye in pyridine or acetic acid being red. That this sensitivity is not caused by the presence of the *meso*phenyl group *per se* is shown by the dihydrochloride of I (R = $CH_3$) and the monohydrochloride of I (R = $C_2H_5$), giving blue solutions changing to red on basification. The anomaly is attributed by the authors to overcrowding and loss of nuclear planarity. Unlike the phenyl compound, the *meso*alkyl dye bases are unstable, and rapidly change into carbinol ethers in alcohol, which regenerate the dye salts on acidification.



(I)

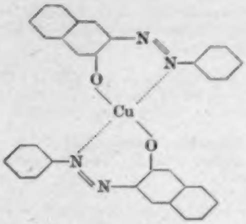
H. H. H.

**Colour in relation to the Chemical Constitution of the Metallic Derivatives of *iso*Nitrosomalonylguanidine.** R. L. Handa and S. Dutt. *J. Indian Chem. Soc.*, **27**, 647–650 (Dec. 1950).

Twenty metallic derivatives (K, Li, Ca, Ba, Mg, Zn, Cd, Hg, Al, Pb, Bi, Mn, Co, Ni, $Fe^{++}$, $Fe^{+++}$, Cu, U, Ce, and Th) of *iso*nitrosomalonylguanidine have been prepared by the interaction of the potassium salt with various other metallic salts in aqueous solution. All are brightly coloured substances with hues differing from each other, and their stability, insolubility in water, and solubility in organic solvents indicate them to be internal metallic complexes. H. H. H.

**2:3-Benzeneazonaphthol.** H. E. Fierz-David, L. Blangey, and E. Merian. *Helv. Chim. Acta*, **34**, 846–853 (May 1951).

2:3-Benzeneazonaphthol, prepared by reaction of 2:3-aminonaphthol with thionyl chloride and disproportionation of the product with phenylhydroxylamine, is orange-yellow in colour, in striking contrast with known benzeneazonaphthols; it affords a copper complex—



and behaves as an azo compound and not as a hydrazone. The hydroxyl group no longer functions as an auxochrome in the Witt sense. The existence of metallic complexes is held to be no proof for the formulation of benzeneazonaphthols with hydrogen bonds, and the union of the copper with the nitrogen atom has the nature of a subsidiary valency. H. H. H.

**Azo Dyes from 2:8-Aminonaphthol and some of its Derivatives. I—Azo Dyes from 2:8-Aminonaphthol.** V. V. Perekalin and N. M. Slavachevskaya. *J. Gen. Chem.* (*U.S.S.R.*), **21**, 897–908 (May 1951).

2:8-Aminonaphthol couples with diazotised aniline giving mainly 1-benzeneazo-2:8-aminonaphthol under acid conditions and mainly 5-benzeneazo-2:8-aminonaphthol under alkaline conditions. The first dye will not diazotise, and its absorption maximum in alcoholic soln. is not affected by the addition of caustic soda; it forms a chromium lake. These and other properties are explained by the occurrence of bonding through the hydrogens of the hydroxyl and amino groups to the nitrogens of the azo link. In the second dye the $NH_2$ and OH show their normal properties. This dye will couple further with diazotised aniline to give 5:7-dibenzeneazo-2:8-aminonaphthol. A. E. S.

**Selective Diffusion into Ion-exchange Resins. A New Method for the Purification of the Direct Cotton Dyes.** R. W. Richardson. *J.C.S.*, 910–914 (April 1951).

The purifications of direct cotton dyes now described are made by an ion-exchange technique, and are based upon the fact that the ion-exchangers used are capable of acting as "molecular sieves". This observation, that selective diffusion of ionic species into the bulk of the resin structure depends on the molecular dimensions of the ion, is utilised for the effective separation of the large organic anions of the dye from those of the much smaller diluent salts. With dyes yielding water-insoluble sulphonic acids, exchange from aqueous–organic solvents was unsatisfactory, and for these and for "acid-labile" dyes the alternative "reverse deionisation" using strongly basic exchangers was employed. Comprehensive details are given for Sky Blue FF (*C.I.* 518), and results are cited for pure Benzopurpurin 4B (*C.I.* 448), Chlorazol Fast Red (*C.I.* 419), and sodium 8-acetamido-1-hydroxy-2-phenylazonaphthalene-5-sulphonate. H. H. H.

**Stoichiometry and Extinction Data of Solutions of Alizarin Lakes of Cations of the Titanium Series.** Y. Dorta-Schaeppi, H. Hürzeler, and W. D. Treadwell. *Helv. Chim. Acta*, **34**, 797–805 (May 1951).

The stoichiometry is investigated of the coloured lakes arising in dilute weakly acid solution from alizarinsulphonic acids with $Al^{3+}$, $Sn^{4+}$, $Ti^{4+}$, $Zr^{4+}$, $Hf^{4+}$, and $Th^{4+}$, and the stabilities of the complexes are established for the pH range 4–10. Their extinction maxima are displaced independently of the radius of the cation, and the displacements are in accord with Kuhn's absorption theory (*Helv. Chim. Acta*, **31**, 1441 (1948) ). In analogous manner, the extinction maximum of the ferric salt of benzhydroxamic acid is in agreement with the calculated value from the structural formula. H. H. H.

**Some Hydroxyanthraquinones and Derivatives.** L. H. Briggs and G. A. Nicholls. *J.C.S.*, 1138–1139 (April 1951).

The following compounds have been prepared by new methods or modifications of existing methods— 2:6-dihydroxyanthraquinone (33% yield) from 2:6-diaminoanthraquinone by diazotisation and replacement of the diazo by the hydroxyl group; 2:6-dimethoxyanthraquinone from the former by means of methyl sulphate and anhydrous potassium carbonate in dry acetone; anthrachrysone (1:3:5:7-tetrahydroxyanthraquinone) by heating an equimolecular mixture of *m*-hydroxybenzoic acid and 3:5-dihydroxybenzoic acid with 10 mol. of conc. $H_2SO_4$ for 1 hr. at 100°c. with chromatographic separation of the product on a magnesia column, also its tetra-acetate, tetrabenzoate, and 3:7-dimethyl and tetramethyl ethers; and purpurin trimethyl ether from purpurin by the above method. H. H. H.

**Purpurogallin.** *J.C.S.*, 1313–1327 (May 1951).

V—Some Improvements in Synthetical Methods. D. Caunt, W. D. Crow, and R. D. Haworth (pp. 1313–1318).

VI—Mechanism of the Oxidation of Pyrogallol. A. Critchlow, R. D. Haworth, and P. L. Pauson (pp. 1318–1325).

VII—Constitution of Purpurogallincarboxylic Acid. W. D. Crow and R. D. Haworth (pp. 1325–1327).

**Cyanine Dyes containing the Pyrrocoline Nucleus—I.** F. G. Holliman and H. A. Schickerling. *J.C.S.*, 914–920 (April 1951).

2-Methyl-3-nitroso-, 3-nitroso-2-phenyl-, 3-acetyl-2-methyl-1-nitroso-, and 3-acetyl-1-nitroso-2-phenylpyrrocoline have been condensed with *α*-picoline methiodide, quinaldine methiodide, and 2:3:3-trimethylindolenine methiodide, to give twelve azadimethincyanines. A further range, with wider variation in the non-pyrrocolinyl nucleus, has been obtained by condensing 1- and 3-nitroso-2-phenylpyrrocoline with 6-ethoxy-2-methylquinoline ethiodide, 2-methyl-5:6-benzoquinoline methiodide, and 2-methylpyridino(2′:3′-5:6)quinoline methiodide. Light absorptions of these dyes are given and discussed. H. H. H.

**Yield of Dye in Colour Development.** A. N. Iordansky and G. I. Arbuzov. *J. Appl. Chem.* (*U.S.S.R.*), **24**, 337–340 (March 1951).

In a further investigation of the formation of azomethin dyes in photographic colour development (cf. J.S.D.C., **67**, 35 (Jan. 1951) ), it is shown, by examining the development of a commercial bluish-red component, that the amount of metallic silver formed during development is 4 g.-atoms per mole of dye formed, which confirms the equation proposed for the reaction—

$$R^1_2N{\cdot}C_6H_4{\cdot}NH_2 + H_2CR^2R^3 + 4Ag^+ \rightarrow R^1_2N{\cdot}C_6H_4{\cdot}N{:}CR^2R^3 + 4Ag + 4H^+$$

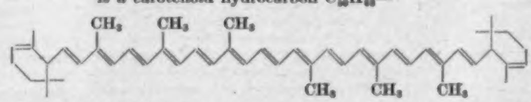
Within the limits found in practice, the grain size of the emulsion does not affect the yield of dye. A. E. S.

**Pigments of *Penicillium herquei*.** F. H. Stodola, K. B. Raper, and D. I. Fennell. *Nature*, **167**, 773–774 (12th May 1951).

Analytical data and some chemical and physical properties of a red pigment isolated from *Penicillium herquei* are reported. W. K. R.

**Syntheses of Carotenoids. VII—Synthesis of Decapreno-$\varepsilon_1$-carotene.** P. Karrer, C. H. Eugster, and M. Faust. *Helv. Chim. Acta*, **34**, 823–826 (May 1951).

Decapreno-$\varepsilon_1$-carotene, whose synthesis is now described, is a carotenoid hydrocarbon $C_{50}H_{68}$—



which is distinguished from the isomeric decapreno-*β*-carotene by containing two *α*-ionone instead of two *β*-ionone rings, and is a higher isoprene homologue of $\varepsilon_1$-carotene. H. H. H.

**Colour of Gold Hydrosols.** L. de Brouckère, A. Watillon, and M. Rémont. *Bull. Soc. chim. Belg.*, **60**, 11–20 (Jan.–March 1951).

The colour of hydrophobic gold hydrosols is not determined by particle size alone; for a given size the absorption spectrum depends largely on the concentration of reagents used for the preparation of the sol. Relatively stable blue hydrosols result with concentrated reagents by the nuclei

method, whilst red or violet sols of the same dispersity appear when dilute reagents are used. H. H. H.

**Colour Change from Red to Blue of Gold Hydrosols during Coagulation.** L. de Brouckère, A. Watillon, and F. Van Grunderbeeck. *Bull. Soc. chim. Belg.*, **60**, 21–25 (Jan.–March 1951).

When a gold hydrosol is coagulated by an electrolyte, the accompanying colour change from red to blue cannot be ascribed to an increase in particle size, since it occurs instantaneously on addition of the electrolyte even for extremely slow coagulation. H. H. H.

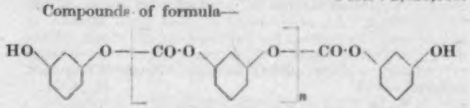
PATENTS

**Sulphonamide Azo Coupling Components.** General Aniline & Film Corpn., S. C. Slifkin, and T. J. Trojnar. *U.S.P.* 2,537,098.

Compounds of formula $X{\cdot}SO_2{\cdot}NR^1R^2$ (X = any organic nucleus capable of coupling; $R^1$ and $R^2$ = H, Alk, hydroxyalkyl, etc.) are couplers for diazotype compositions which yield prints of good wash fastness. They have affinity for cellulose esters. C. O. C.

**Resorcinol Derivatives as Coupling Components in Diazotype Printing.** General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. *U.S.P.* 2,536,989.

Compounds of formula—



($n$ = 0 or a whole number) used as azo couplers have good precoupling stability and yield sepia images of good density and high actinic opacity. C. O. C.

**Polyacetoacetyl Derivatives of Polyamines as Azo Components.** General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. *U.S.P.* 2,537,106.

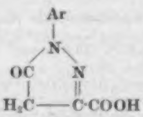
Polyacetoacetyl derivatives of aliphatic, aromatic, or heterocyclic polyamines are especially effective as azo components for diazotype compositions. C. O. C.

**Phenolic Colour Formers.** du Pont and A. B. Jennings. *U.S.P.* 2,537,138.

Polymers useful as colour formers are obtained by treating a monohydric phenol with an ether of an alkylolamide in a solvent or diluent in presence of an acidic condensing agent. C. O. C.

**Pyrazolone Diazotype Couplers.** General Aniline & Film Corpn. and S. C. Slifkin. *U.S.P.* 2,536,398.

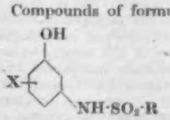
Compounds of formula—



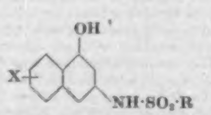
couple with diazotised *p*-diamines of the benzene series to yield deep reds of good light fastness and excellent wash fastness. C. O. C.

**Colour Formers for Azine Dyes.** General Aniline & Film Corpn., W. A. Schmidt, and J. A. Sprung. *U.S.P.* 2,536,010.

Compounds of formula—



or



(R = Alk or Ar; X = H, Alk, or sulpho) form azine dyes with the oxidation products of primary aromatic amino developers. C. O. C.

**Blue, Chromiferous, Monoazo Dye for Wool, etc.** Ciba Ltd. *B.P.* 653,525.

Blues and navy blues of good appearance in artificial light are given on wool, nylon, etc. by the dye obtained by treating the monoazo compound 1-amino-2-naphthol-4-sulphonic acid→1-naphthol-5-sulphonic acid with a salt of tervalent chromium, e.g. the sulphate. E. S.

**Substantive, Copperable, Disazo Dyes.** Ciba Ltd. *B.P.* 654,491.

Mainly blue substantive dyes which may be coppered in substance or on the fibre are made by tetrazotising a 3:3′-dialkoxybenzidine and coupling with 1 mol. of a 1-naphtholtrisulphonic acid (especially the 3:6:8-trisulphonic acid) and 1 mol. of a coupling component free from sulpho groups and capable of coupling in a position *ortho* to an OH group. The coppering in substance is done under conditions in which the alkoxy groups are split off. Thus dianisidine is tetrazotised and coupled first with 1 mol. of 1-naphthol-3:6:8-trisulphonic acid in presence of soda ash, and then with 1 mol. of 2-hydroxy-3-naphthoic anilide in presence of caustic soda and pyridine. The coupling mixture is heated at 80–90°C. with ammoniacal copper sulphate to produce the copper complex, which dyes cotton greenish blue. E. S.

**Dyes and Pigments derived from Thiazolyl-2-thioglycollic Acids.** Ilford Ltd., G. F. Duffin, and J. D. Kendall. *B.P.* 654,346.

The products obtained by the process of *B.P.* 643,681 (J.S.D.C., **67**, 38 (Jan. 1951) ) or their acyl compounds are treated with an alkyl, aralkyl, or alkylene halide in alkaline medium. The resulting pigments are insoluble in all the normal inorganic and organic solvents. C. O. C.

**Trinuclear Azacyanine Dyes.** General Aniline & Film Corpn. and H. G. Derbyshire. *U.S.P.* 2,535,982.

Trinuclear cyanine dyes, containing an aza group in the chromophoric chain, are prepared in excellent yield and readily purifiable form by treating a *cyclo*ammonium quaternary salt, of the type usually employed in cyanine dye syntheses, with an azathiazolone cyanine dye in a suitable solvent and in presence of a basic condensing agent, either at room temperature for 1 hr. or by boiling or refluxing for a few min. C. O. C.

**Rendering Acetate Rayon Dyes readily Dispersible.** British Celanese Ltd. *B.P.* 654,795.

Insoluble acetate rayon dyes are milled with water, a water-soluble salt of a ligninsulphonic acid, and a neutral or alkaline inorganic salt of a univalent cation which does not form an insoluble soap. The milled paste is then dried and ground. The products disperse readily in water to yield dye dispersions free from sediment and stable over long periods. C. O. C.

**Carbon Black.** M. Steinschlaeger. *B.P.* 654,081.

Improved quality and higher yield are obtained by mixing a hot gas with a hydrocarbon-containing material at a temperature insufficient to crack it to carbon black, passing it to a place where it is mixed with another hot gas to bring the average temperature to 800–1400°C., and then cooling in < 5 sec. to a temperature at which reaction between the resultant carbon black and $CO_2$ and steam does not take place. C. O. C.

**Collection of Carbon Black.** Research Corpn. and C. W. J. Hedberg. *B.P.* 654,350.

The stream of hot air laden with carbon black from a furnace passes first through a dry collecting zone and then through a wet collecting zone, where a major portion of the residual entrained carbon black is separated in contact with water. An aqueous slurry of the carbon black collected in the wet zone is injected into the hot furnace gas at any point between the furnace and the down-stream end of the dry collecting zone. This evaporates the water and leaves the carbon black suspended in the gas stream. Higher yields are obtained. C. O. C.

**Hardened Carbon Black Pellets.** Phillips Petroleum Co. and M. L. Studebaker. *U.S.P.* 2,538,482.

**Bright Red Iron Oxide Pigment.** I.C.I. Ltd., P. J. Atkins, J. B. Peel, and S. E. Scrimshaw. *B.P.* 653,358.

Modification of *B.P.* 635,177 (cf. J.S.D.C., **66**, 388 (1950) ); a zinc and/or aluminium compound may replace the magnesium compound. C. O. C.

**Ultramarine.** Interchemical Corpn., A. E. Gessler, and C. A. Kumins. *U.S.P.* 2,535,057.

A mixture of artificial zeolite, sodium sulphide or polysulphide, and excess sulphur is heated under reducing conditions for 2–4 hr. at 750–850°C., cooled to 475–625°C., kept at that temperature for not < 1 hr. in an oxidising atmosphere in presence of sulphur oxides, and finally cooled and washed. C. O. C.

**Guanylmelamines and Acid Salts thereof— Flame-proofing Agents and Intermediates for Dyes and Textile Agents.** American Cyanamid Co. (III, p. 348.)

## V—PAINTS; ENAMELS; INKS

**Polymers and Copolymers— Coating Compositions.** Monsanto Chemical Co. and G. R. Barrett. (III, p. 348.)

## VI—FIBRES; YARNS; FABRICS

**Cause of Damage to Natural Fibres by Micro-organisms— I.** W. Wegener and R. Questel. *Melliand Textilber.*, **32**, 346–349 (May 1951).

A list is given of the various fungi which have been detected on textiles composed of the natural fibres. There are 76 literature references. F. A.

**Refinement of the Tub Model of Cellulose (Problem of the Cellulose Modifications— II).** A. Sippel. *Kolloid-Z.*, **122**, 20–23 (April 1951).

The tub model for cellulose, previously proposed for the interpretation of the X-ray diagram, is now modified so that the length of the cellobiose unit becomes 10·3 A. There is also a second main form of the tub model. H. H. H.

**Effect of Low Degree of Alkylation on the Properties of Cellulose Fibres.** N. I. Nikitin and N. I. Klenkova. *J. Appl. Chem. (U.S.S.R.)*, **24**, 296–307 (March 1951).

Cotton linters were impregnated with a 17·5% soln. of caustic soda and then treated with the vapour of methyl iodide, ethyl iodide, or ethylene oxide to give either a methyl, ethyl, or hydroxyethyl deriv. of cellulose. The product was compared with the original cellulose and with cellulose that had been treated with caustic soda only. Measurements were made of hygroscopicity and of rate of hydrolysis by acid. Owing to progressive hydrogen-bond breakdown, hygroscopicity and particularly hydrolysability increase with increasing alkylation up to a certain limit. Thus the extent of hydrolysis, estimated by the amount of reducing sugar formed in soln. during an 8-hr. boil with 5% $H_2SO_4$, was 10% for the original cellulose, 21% for the alkali-treated cellulose, and 80% for methylated cellulose (7–8% $CH_3$). At a given alkyl content methyl cellulose and hydroxyethyl cellulose differ only slightly with respect to the properties measured, but ethyl cellulose is less hygroscopic and much less readily hydrolysed. This suggests that not only the size of the substituent group, but also its hydrophobic or hydrophilic nature, is of importance in determining the effect of its introduction on the properties of cellulose. The results obtained were shown to be substantially independent of the degree of polymerisation of the cellulose preparation used. A. E. S.

**Action of Alkalis on Cellulose.** A. Schaeffer. *Textil-Rund.*, **6**, 159–168 (April) and 219–225 (May 1951).

Cotton and regenerated celluloses were treated with various alkalis at the boil and examined by physical, chemical, and microscopical methods for damage. The results show that the effect is independent of the liquor ratio used, but the degree of degradation depends on the type of fibre and the nature and concn. of alkali. The alkalis examined can be placed in the following order with respect to degree of degradation produced— caustic soda > sodium monosilicate > soda ash > sodium disilicate, sodium trisilicate, and water glass > water. No relationship between pH and degree of damage was established, but with two soln. of different alkalis of the same alkali concn., that with the higher pH value shows more damage. The max. absorption of alkali at the boil corresponds to 0·584 g. $Na_2O$ per litre, which represents 1 g. $Na_2CO_3$ per litre. B. K.

**Effect of Partial Acetylation on Jute.** W. G. Macmillan and A. B. Sen Gupta. *Nature*, **167**, 775 (12th May 1951).

A study has been made of the relative amounts of acetyl groups which react with the individual fibre components when jute is partly acetylated. From the results obtained it is considered that the hemicelluloses react with more acetyl groups than lignin, whilst the cellulosic component takes up only a small amount of acetyl. W. K. R.

**Electron-microscopic Study of Viscose Rayon Fibres.** K. Mühletaler. *Experientia*, **6**, 226 (June 1950): *Melliand Textilber.*, **32**, 357 (May 1951).

Electron-microscopic studies on macerated viscose rayon fibres show the presence of microfibrils and residues of the native cellulose together with structural elements which have been formed during coagulation of the viscose. It is concluded that, in the manufacture of viscose rayon, the native cellulose first dissolves to give a polydisperse system, and then on coagulation the more completely dissolved parts of the cellulose act as a cement for those parts which have remained in a more aggregated state. F. A.

**Investigation of the Diagnostic Physical Properties of Rayons by E. Elöd's Method.** P. H. Hermans. *Kolloid-Z.*, **122**, 1–5 (April 1951).

E. Elöd's method for the layerwise scaling of rayon fibres, by repeated acetylation and removal of the acetate layers, has been applied to follow microscopically the variation of the physical properties of rayons from the exterior to the centre. For viscose rayon, a density increase and an orientation decrease were established from without to within, while an X-ray determination of degree of crystallinity showed no difference. In one case at least, the increase of density could be traced by electron- and photo-microscopic observations to a porous structure of the fibre coating. An orientation increase from without to within was established for cuprammonium rayon. Data are given for two kinds of thick cord rayon, three varieties of ordinary viscose rayon, and one Bemberg cuprammonium rayon. H. H. H.

**Double Refraction of Artificial Fibres.** G. Bozza and E. Bonauguri. *Kolloid-Z.*, **122**, 23–34 (April 1951).

A mathematical investigation of the distribution of the index of double refraction in artificial fibres, viz. nylon and cuprammonium rayon. H. H. H.

**Turbidimetric Titration of Cellulose Acetate.** J. Bischoff and V. Desreux. *Bull. Soc. chim. Belg.*, **60**, 137–155 (Jan.–March 1951).

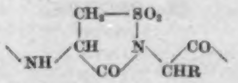
Modifications of technique in the turbidimetric titration of polymers are described and their advantages are discussed. The system butanone–ethanol is found to be very suitable for the titration of cellulose acetate. The average size of the micelles is shown to remain constant during the course of the titration, but varies from one fraction to another, and the hypothesis is advanced that in the crude product there is a substance which stabilises the micelles and whose concentration varies with the fraction. The conversion of the turbidimetric titration curves to those of molecular distribution is discussed. H. H. H.

**Observations on the Subcuticle Membrane in Wool Fibres.** N. Gralén, G. Lagermalm, and B. Philip; P. Alexander and H. Haselmann. *Melliand Textilber.*, **32**, 350–352 (May 1951).

The membrane which Alexander has isolated from wool fibres by treatment with peracetic acid (*ibid.*, **31**, 385 (1950) ) is shown by electron-microscopic examination to consist of parts of the cuticle together with the outer and more resistant cells of the cortex. This observation is discussed and a reply made by Alexander and Haselmann. F. A.

**Relationships between Structure and Chemical Reactivity of Wool Fibres.** P. Alexander. *Kolloid-Z.*, **122**, 8–19 (April 1951).

It is shown that, by oxidation of the disulphide bonds with peracetic acid, 90% of the wool fibre can be brought into solution without disintegration of the main chains. The insoluble part is the "intermediate membrane" of Elöd and Zahn, and the soluble portion consists essentially of $\alpha$-keratose of mol. wt. $\sim$ 70,000 and $\gamma$-keratose $\sim$ 4500. $\alpha$-Keratose gives an X-ray diagram which is typical of $\alpha$-folding proteins, while $\gamma$-keratose is in the $\beta$-configuration. It is found that in manufactured fibres the $\alpha$-folding is much less stable than in the natural wool fibre, and it is concluded that the disulphide bond contributes substantially to the stability of the $\alpha$-folding. It is shown that $\alpha$-keratose may be transformed into a protein which gives a $\beta$ X-ray pattern, and in this form it is appreciably less soluble. By oxidation of the disulphide bond, the formation of two cysteic acid groups is hindered by steric factors, and the heterocyclic imide—



is formed; this is decomposed by alkali giving a sulphonamide –NH·CH(COOH)·$CH_2$·$SO_2$·NH·CHR·CO–, which is stable towards normal protein hydrolysis, but which may be hydrolysed under more severe conditions. It follows from the present experiments that the cystine in wool is combined with each amino acid. 75% of the cystine and 70% of the tyrosine in wool do not react with hypochlorite and acid permanganate, although the total cystine and tyrosine are oxidised by chlorine, a difference attributed to the concurrent reactions of the hypochlorite with the low-mol.wt. phase, $\gamma$-keratose. The number of carboxyl groups accessible to esterification by different alcohols depends on the dimensions of the latter, while only 60–70% of the tyrosine is accessible to fluorodinitrobenzene. A model is proposed for the macromolecular structure of wool, which accords with the theories of Astbury and Woods and of Elöd. H. H. H.

PATENTS

**Spinning of Unripened Viscose.** du Pont and N. L. Cox. *U.S.P.* 2,535,044, *U.S.P.* 2,535,045, *U.S.P.* 2,536,014.

**Regeneration of Cellulose from Viscose.** du Pont. *B.P.* 654,083.

Smooth-surfaced filaments of high tenacity and high fatigue resistance and with improved resistance to soiling and abrasion are obtained by extruding viscose into aq. $H_2SO_4$ containing 1–15% $ZnSO_4$ and stretching the resultant filaments. The viscose used must contain per 100 g. < 1 millimole of a $C_4$–$C_6$ monoamine soluble to at least 0·3% in 6% aq. NaOH. C. O. C.

**Preventing Degradation of Acid-moist partly Regenerated Cellulose.** American Viscose Corpn., W. A. Sisson, and M. M. Cruz, Jr. *U.S.P.* 2,538,279.

When acid-moist partly regenerated cellulose is stored equilibrium can be established between the rate at which dexanthation is completed and the rate of acid degradation, by keeping the goods at pH 2·5, when acid degradation is completely inhibited irrespective of other conditions, e.g. temperature and time of storing. C. O. C.

**Wet Spinning of Cellulose Acetate.** Courtaulds Ltd., L. A. Bashford, and G. Doubleday. *B.P.* 652,844.

Threads of good tensile strength are obtained by extruding a solution of cellulose acetate into an aqueous bath containing > 20% potassium acetate. W. G. C.

**Dyed and Crimped Staple Fibre.** British Celanese Ltd. *B.P.* 653,575.

A tow of continuous filaments of an organic derivative of cellulose is dyed, crimped, and then cut into staple fibre. C. O. C.

**Cellulose Acetate Staple Fibres.** Courtaulds Ltd., L. A. Bashford, and G. Doubleday. *B.P.* 652,845.

Staple fibres of cellulose acetate are produced by extruding into an aqueous coagulating bath an aqueous acetic acid solution of cellulose acetate (obtained directly by esterification of cellulose) through one or more jets having at least 1500 holes, collecting the filaments to form a tow of substantially parallel fibres, cutting the wet tow into staple lengths, and drying the cut fibres in bulk. W. G. C.

**Insolubilising Artificial Protein Filaments.** I.C.I. Ltd., W. E. Tetlow, and R. H. K. Thomson. *B.P.* 654,513.

Artificial protein, e.g. peanut or casein, filaments are relaxed after coagulation and then hardened by treating in formalin containing not < 240 g. NaCl per litre at pH 4–7 and not > 80°c., and then in strongly acid formalin containing 250–325 g. $H_2SO_4$ and 370–480 g. $Na_2SO_4$ per litre at 70–98°c. J. W. B.

**Antistatic Agents for Incorporation in Polyvinylidene Chloride Compositions.** Dow Chemical Co., J. S. Gowing, C. B. Havens, E. D. Serdynsky, and R. M. Wiley. *U.S.P.* 2,537,712.

Incorporation into polyvinylidene chloride of 0·5–5·0% by weight of a mono-*n*-butyl, mono-*n*-amyl, or monoisoamyl adipate greatly reduces the formation of static. C. O. C.

**Acrylonitrile Copolymers suitable for making Fibres.** American Viscose Corpn. and D. W. Chaney. *U.S.P.* 2,537,031.

**Sighting of Nylon.** I.C.I. Ltd., N. A. Armitage, and J. Henderson. (VII, this page.)

**Combination of Acids and Dye Acids with Wool.** H. Gerstner. (VIII, p. 354.)

**Bacterial Damage to Textiles and its Prevention.** M. Nopitsch. (X, p. 355.)

**Structure and Properties of Cellulose, its Esters, and its Ethers. XXXII—Conditions for the Interconversion of Native and Hydrate Cellulose.** M. Ginzberg and Z. Rogovin. (XI, p. 356.)

## VII—DESIZING; SCOURING; CARBONISING; BLEACHING

**Removal of Wool Spinning Oils by Scouring.** M. Kehren. *Melliand Textilber.*, **32**, 394–399 (May 1951).

Communication No. 4 of the Technical Committee of the Gesamtverband der deutschen Textilveredlungsindustrie. Test methods are given for determining the ease of emulsification of spinning oils and their content of saponifiable and unsaponifiable matter, water, and free fatty acid. The ease with which oils may be removed from wool yarn or strips of fabric is determined by scouring by hand or in a laboratory machine. Results are given for a number of different types of oil and with various scouring recipes. F. A.

PATENT

**Sighting of Nylon.** I.C.I. Ltd., N. A. Armitage, and J. Henderson. *B.P.* 653,221.

Inorganic pigments used for sighting nylon are readily scoured out even after steaming under pressure. C. O. C.

## VIII—DYEING

**Research on the Dyeing of Synthetic Fibres.** T. Vickerstaff. *Teintex*, **16**, 165–171 (April 1951).

The behaviour of direct cotton dyes is studied on cotton and cuprammonium and viscose rayons with respect to heat of dyeing, affinity at various temp., time of half dyeing, and degree of exhaustion. Established principles involved in the dyeing of nylon and Terylene are discussed. B. K.

**Dyeing Cotton with Vat Dyes.** J. A. Fowler, A. G. H. Michie, and T. Vickerstaff. *Melliand Textilber.*, **32**, 296–302 (April 1951).

The application of 1-benzoylaminoanthraquinone, 1:4- and 1:5-dibenzoylaminoanthraquinone, flavanthrone, and pyranthrone in leuco form to cotton has been studied under controlled conditions. With dyeing times of 1–3 weeks at 40°c. and with ion concn. of 0·15–0·30 N., adsorption isotherms were plotted, whose thermodynamic evaluation led to the explanation of the affinities of dyes for cellulose fibres as the difference in the chemical potential between the state of the dyes in the liquor and dyes in the fibre. Dyeing of cellulose with vat dyes proceeds in the same manner as with direct dyes, involving the adsorption of dye anions, and the distribution of sodium ions between fibre and dye liquor obeys the laws of membrane equilibrium. The differences in dyeing behaviour between vat and direct dyes are based on the high electrolyte content of the average vat dyebath. It is concluded that leuco vats are not aggregated to any appreciable extent at 40°c. in spite of the high salt concentration. B. K.

**Vat Dyeing.** R. Haller. *Helv. Chim. Acta*, **34**, 793–797 (May 1951).

Previous work (*Melliand Textilber.*, **6**, 664 (1925); *Cellulosechemie*, **6**, 189 (1925); *Helv. Chim. Acta*, **17**, 761 (1934)) is continued on the phenomenon of "physical condensation", and the cause of dye migration and its crystallisation in the lumen of the cotton fibre. For this purpose viscose rayon, which acquires hollow spaces during the spinning process, is dyed with indigo, and the

same phenomenon obtained as for natural cotton fibres. It is tentatively concluded that purely physical influences such as temperature and pressure are responsible for the phenomenon. H. H. H.

**Theory of Wool Dyeing with Acid and Direct Dyes.** H. G. Fröhlich. *Melliand Textilber.*, **32**, 307–311 (April 1951).

A review, with 35 references to the literature, of the theories suggested to explain the dyeing of wool and other protein fibres. B. K.

**Combination of Acids and Dye Acids with Wool.** H. Gerstner. *Melliand Textilber.*, **32**, 388–391 (May 1951).

A review of the literature on the mode of combination of acids and dye acids with wool. Support is lent to the views expressed by Ender and Müller, and Valko, according to which a dye acid is bound to wool by a linkage additional to the salt link such as obtains with simple acids. It is suggested that this additional linkage occurs between the carboxyl group in wool and the azo group in the dye. F. A.

**Dyeing of Chrome Leather with Anionic Dyes.** G. Otto. *Melliand Textilber.*, **32**, 311–314 (April 1951).

Modern theories of chrome leather dyeing with acid and direct dyes are reviewed. Experiments are described comparing the uptake of acid and direct dyes by columns of collagen fibres, electrolyte-free chromic hydroxide, and chrome leather. It was found that increase in molecular size and number of chromophoric groups in the molecule of anionic dyes resulted in increase in affinity between dye and chrome leather. This serves to explain the observation that, when chrome leather is retanned with vegetable tannins and is subsequently dyed with anionic dyes, those dyes which exhibit high affinity for pure chrome leather now show just as low affinity as dyes of low mol. wt. It is also possible to explain the effect of drying leather on its subsequent affinity for dyes. B. K.

PATENTS

**Dyeing with Metallised Azo Dyes — Improved Brightness.** Ciba Ltd. *B.P.* 654,023.

Metallised azo dyes, especially chromium complexes of monoazo compounds, e.g. nitro-*o*-aminophenol→2-naphthylaminesulphonic acid, suffer less degradation, and hence give brighter hues, if dyeing is conducted in presence of an aldehyde containing a carboxyl or sulpho group. Thus, in dyeing wool with 1·5% of the chromium complex of 5-nitro-2-aminophenol→2-naphthylamine-6-sulphonic acid, purer, yellower greens are produced if 3% of monosodium benzaldehyde-2:5-disulphonate is included in the dyebath. E. S.

**Dyeing Hair, Fur, etc. with Melanin by the use of physiologically occurring Propigments.** S. M. Peck. *U.S.P.* 2,539,202.

The material is dyed with a solution of dihydroxyphenylalanine or tyrosine, preferably in presence of oxidase or tyrosinase, and then dried and oxidised. C. O. C.

**$\gamma$-Valerolactone and $\gamma$-Butyrolactone as Assistants in Dyeing Acetate Rayon, Vinyl Resin Fibres, etc.** Monsanto Chemical Co., S. U. Shorey, and G. W. Wright. *U.S.P.* 2,535,098.

Cellulose esters and ethers, synthetic resin fibres, etc. can be continuously dyed by passing them through a bath of 5–35% (by vol.) aq. $\gamma$-valerolactone or $\gamma$-butyrolactone at 20–45°C. containing in suspension a dye having affinity for the fibre. The material must be washed off within 50 sec. of entering the dye liquor, the higher the proportion of lactone in the liquor the shorter being this interval. The dye does not exhaust from the liquor, which merely needs keeping to level. C. O. C.

**Dyeing Vinyl and Vinylidene Resins with Acid and Direct Dyes dissolved in Glycol Ethers and Esters.** American Viscose Corpn. and J. A. Woodruff. *U.S.P.* 2,537,177.

The material is dyed below its shrinking temperature with an acid or direct dye dissolved in the anhydrous monoethyl, monomethyl, or monobenzyl ether of ethylene glycol, the monomethyl or monoethyl ether of diethylene glycol, or diethylene glycol monoacetate, and then washed off in water. C. O. C.

# IX—PRINTING

PATENTS

**Printing Pastes.** Girdler Corpn. *B.P.* 653,244.

Modification of *B.P.* 649,324 (J.S.D.C., **67**, 197 (May 1951)). An aqueous slurry of the ingredients is continuously fed through a zone where uniform and simultaneous heating of all portions of the slurry present in the zone is effected. The slurry is heated to that temperature at which its state of disorganisation is such that maximum viscosity of the starch is obtained. The paste is then passed to a cooling zone, where it is rapidly cooled to below cooking temperature so as to maintain the state of disorganisation obtained in the heating zone. This gives a paste of desired body with the use of much less starch than has hitherto been required. C. O. C.

**Printing Textiles by use of Light-sensitive Diazo Salts.** General Aniline & Film Corpn. and S. C. Slifkin. *U.S.P.* 2,537,097.

Prints of excellent gradation and density are produced on all types of textiles by impregnating them with a mixture of (1) a diazonium compound of an aromatic amine which is decomposed by light to yield a non-coupling compound, (2) a compound which couples in alkaline medium, (3) a precoupling preventive, and (4) $ZnCl_2$; exposing to light through a negative; and then developing in alkali. C. O. C.

**Photographically Producing Multicoloured Designs on Cloth, Paper, etc.** Calico Printers' Assocn. Ltd., F. Isherwood, and W. S. Miller. *B.P.* 653,698.

A multicolour design is produced on cloth, paper, or other sheet material by treating it with a composition which forms a dye on exposure to light, treating with a desensitiser, and then applying another light-sensitive coating, this cycle of operations being repeated for each colour required. The whole process is completed before the material is washed and while it is held so that no alterations in dimension can occur. Preferably all the light-sensitive compositions used contain a desensitiser for the previously applied composition. If desired the last composition applied comprises an alkali-metal chromate which on exposure to light in presence of an alkali and a reducing agent forms a mordant, which is dyed after the material has been washed. C. O. C.

**Silk Screen Printing on Metal using Paints or Inks containing Synthetic Resins.** N. L. Cowling and A. W. Woolven. *B.P.* 653,842.

The inks used consist of pigments dispersed in a urea- or melamine–formaldehyde resin plasticised with an alkyd resin. The background colour is first painted on and then stoved until hardened; one colour of the design is then printed on and stoved, after which another colour of the design is applied and stoved, this process being repeated until the whole of the multicolour design is applied. Finally a coating of the same ink but not containing a pigment is applied and stoved. The printed metal can be bent or struck without rupture of the printed surface. C. O. C.

**Figured Effects on Cellulosic Textiles.** J. M. Fussenegger, A. Fussenegger, H. Fussenegger, J. Fussenegger, S. Ginzel, A. Rhomberg, and H. Wührer. *B.P.* 653,446.

The fabric is printed with a resist made up of an aqueous emulsion of hydrocarbons, glycerides, waxes or higher fatty acids, a thickening agent which is removed by washing, and a pigment and/or metal salt which forms a pigment by hydrolytic dissociation or thermal decomposition. It is then dried and/or steamed, and finally parchmentised with sulphuric acid. C. O. C.

**Photographic Imbibition Dye Printing Process.** Eastman Kodak Co. and W. J. Weyerts. *U.S.P.* 2,537,924.

Contrast in imbibition dye printing is controlled, particularly at low pH, by adding to the dyebath arylsulphonic acids having a 0–4 C alkyl substituent or their salts, which compete with the dye when incorporated into a matrix for transfer to the imbibition dye printing blank. C. O. C.

**Azine Dye Images produced by use of a Developer containing Two *N*-Substituted Diaminometanilic Acids.** General Aniline & Film Corpn. and R. C. Gunther. *U.S.P.* 2,537,460.

**Photographic Sensitised Multicolour Screen.** Société Anonyme Mondiacolor and G. E. Chevalier. *B.P.* 654,504.

**Colour-photographic Reproduction Processes employing Dyed Reliefs.** Kodak Ltd. and D. C. Gresham. *B.P.* 654,164.

**Colour Photography.** Ilford Ltd. and R. R. Robinson. *B.P.* 654,124.

## X—SIZING AND FINISHING

**Bacterial Damage to Textiles and its Prevention.** M. Nopitsch. *Melliand Textilber.*, **32**, 344–346 (May 1951).

Cotton yarns were incubated in solutions containing a pure culture of *Bacillus mesentericus*. The resulting damage to the fibres, which was evaluated by an abrasion test, was found to be small, and did not vary appreciably over the pH range 5·0–8·5. Neither was the damage reduced appreciably by prior treatment of the cotton with chromium salts or antiseptics. It was concluded that the slight damage was caused by hydrolysis during the prolonged incubation and that *Bacillus mesentericus* has no action on cotton. Similar results were obtained with linen, hemp, and viscose, cuprammonium, and acetate rayon. F. A.

**Reaction of Oxidising Agents with Wool. III—Influence of the Morphology on the Rate of Reaction.** P. Alexander, D. Gough, and R. F. Hudson. *Biochem. J.*, **48**, 20–27 (Jan. 1951).

The rate of reaction of wool with aqueous chlorine solutions is constant in the pH range 2–7 but decreases rapidly in the range 8–11. The change in composition of the solution from hypochlorous acid to hypochlorite ions runs parallel with this decrease in rate. The rate-determining process of the reaction of wool with oxidising agents in acid solution is the diffusion of molecules through the fibre to reaction sites, followed by rapid reaction. In alkaline solution, however, the rate-determining stage is neither diffusion through the fibre nor the actual oxidation process but can be interpreted in terms of diffusion across a surface barrier. Recent morphological researches on wool fibres have established the existence of two membranes, one external to the scales (epicuticle) whilst the other forms part of the cuticle (subcuticle). It is shown that the former does not affect the rate of diffusion of the hypochlorite ion, whereas in alkaline solution the negatively charged subcuticle retards the penetration of anions, so that diffusion through this membrane determines the overall rate of reaction. F. F. E.

**Formation by Formaldehyde of a Cross-link between Lysine and Tyrosine Residues in Wool.** P. Alexander, D. Carter, and K. G. Johnson, *Biochem. J.*, **48**, 435–441 (April 1951).

Wool combines irreversibly with formaldehyde at low concentrations in neutral solution at 60°c. with a resultant weight increase of about 0·5%. The formaldehyde-treated wool has an increased resistance to alkali, an increased strength, and a decreased supercontraction in boiling sodium bisulphite. These effects are reversed by hot solutions of pH $< 3$, but not by treatment in alkaline solutions. The tyrosine content falls, whereas the cystine content remains unchanged. If the wool is first acetylated, it does not react with formaldehyde, but oxidation of the cystine linkages or esterification of the carboxyl groups does not inhibit the reaction. It is concluded that formaldehyde forms cross-linkages between the phenyl groups of tyrosine and $\varepsilon$-amino groups of lysine. These are broken by acid without liberation of the formaldehyde, which remains in the wool as hydroxymethyltyrosine. F. F. E.

**Esterification of the Carboxyl Groups in Wool.** P. Alexander, D. Carter, C. Earland, and O. E. Ford. *Biochem. J.*, **48**, 629–637 (May 1951).

The carboxyl groups in wool can be esterified by reaction with alcohols in the presence of acids acting as catalysts. The esterification results in a decrease in acid-combining capacity of the wool, and measurement of this enables the course of the reaction to be followed. The rate of esterification increases with increase of hydrogen ion concentration and of temperature and decreases with increase in the amount of water in the reaction system. The degree of esterification decreases as the molecular weight of the alcohol increases. The ester groups are saponified in 1 hr. in 0·1 N-NaOH at room temperature but not by distilled water at 100°c. The rate of saponification does not depend on the alcohol used for esterification.

Of a number of epoxides only epichlorohydrin was effective in esterifying more than 10% of the carboxyl groups, the optimum pH for the reaction being 5–7. The reaction is accompanied by a large increase (9–10%) in the weight of the wool, and this indicates that extensive reaction with groups other than carboxyl also occurs. Since wool treated with epichlorohydrin can no longer be given a permanent set, it is suggested that this reaction must involve the amino groups.

The esterified wool has an increased affinity for acid dyes in neutral solution and a decreased affinity for basic dyes at all pH values. The fastness to washing of acid dyes on esterified wool is greater than on untreated wool. These changes are in accordance with current views on the mechanism of the absorption of acid dyes by wool (Alexander and Kitchener, *Text. Research J.*, **20**, 203 (1950)).

It is shown that the combination of acids with wool can be accelerated by efficient agitation and that equilibrium can be established in a few minutes. F. F. E.

**Work of E. Elöd on the Weighting of Silk.** F. Vogel. *Melliand Textilber.*, **32**, 376–377 (May 1951).

PATENTS

**Textile Fabrics containing Alkali-soluble Fibres.** I.C.I. Ltd., J. C. Somerville, and J. E. L. Thomas. *B.P.* 653,529.

Fabrics are prepared containing a component which is insoluble, and yarn which is wholly or partly soluble, in weak alkali, the soluble component consisting of an aluminium salt of a cellulose aliphatic hydroxy acid. Subsequent treatment in weak alkali lightens the fabric and gives an open texture. In one example wool is spun to extremely fine worsted yarn (3 parts by wt.) and doubled with a continuous-filament yarn of Al carboxymethyl cellulose (1). A fabric is woven and treated with 1% ammonium hydroxide at 18°c. for 5 min., which dissolves out the Al carboxymethyl cellulose and gives a very lightweight fabric. J. W. B.

**Heat Setting.** Fair Lawn Finishing Co. *B.P.* 653,455.

Nylon cloth is passed in open width at 36–144 yd./min. through a machine, where it is treated for 1–10 sec. by a current of air at 300–500°F. and 400 ft./min. and then immediately cooled. C. O. C.

**Resin Treatment of Cellulosic Textiles.** American Cyanamid Co. and L. A. Fluck, Jr. *U.S.P.* 2,536,050.

Cellulosic textiles are given better resistance to creasing and wrinkling without loss in tensile strength by impregnating them with a melamine–formaldehyde precondensate (1 part) and a film-forming water-soluble thermoplastic polymer or copolymer of a lower alkyl acrylate (1–3), so that on drying they increase 10–30% in weight, and then heat-curing. The process is particularly applicable to mercerised cotton. C. O. C.

**Tracing Cloth.** Monsanto Chemical Co. and H. Wood, Jr. *U.S.P.* 2,537,111.

The base fabric is impregnated with an organic-solvent solution containing (1) a copolymer of a compound of formula R·CH:CH$_2$ (R = subst. or unsubst. phenyl) with a secondary C$_4$–C$_{12}$ Alk half ester of an ethylene-$\alpha\beta$-dicarboxylic acid and (2) a minor proportion of polyvinylbutyral. It is then dried and hot-calendered to glaze it. The product can be used as a non-sensitised tracing cloth, but is particularly suitable for coating with a photographic emulsion, as it can be subjected to aqueous processing without use of an additional water-resistant coating. C. O. C.

**Finishing Fabrics with Water-insoluble Vinyl Resins.** Monsanto Chemical Co. *B.P.* 654,077.

Increase in resistance to wear, laundering, and dry cleaning as well as increased fullness and stiffness are obtained by impregnating the fabric with 1·24–10·0% by weight of a dispersed negatively charged unagglomerated water-insoluble vinyl resin. The dispersion used must be free from other resins and film-forming materials and from cationic surface-active agents, and must have a solids content of 1·02–10·0% by weight. C. O. C.

**Resin-treatment of Endless Felts.** Orr Felt & Blanket Co. *B.P.* 654,079.

The life of papermakers' and other endless felts can be greatly increased by impregnating them with an aqueous solution of a synthetic resin and then heat-curing. Suitable machinery is described. C. O. C.

**Waterproofing Paper Textile Fabrics.** Patchogue-Plymouth Mills Corpn. and J. J. Petroske. *U.S.P.* 2,536,656.

A combined waterproof and lacquered finish is obtained by brush-coating a wax-aluminium acetate emulsion on one side of the fabric, brushing both sides, drying before the fabric is completely impregnated, spraying the untreated side with lacquer under pressure, and allowing the lacquer to dry and form a flexible, transparent, glossy coating. C. O. C.

**Coated Sheet Materials for making Heat-cured Laminates.** N. V. De Bataafsche Petroleum M.-S. and D. W. Elam. *B.P.* 654,475.

Sheets of fibrous material are treated with a mixture of an organic ester of cellulose and a partial polymer of an organic polycarboxylic acid completely esterified with an unsaturated alcohol. They are then formed into laminates by heat-bonding so as further to polymerise the partial polymers present. C. O. C.

**Laminated Felt.** Underfelts Ltd. and A. Kemp. *B.P.* 653,461.

A backing of hessian or other open-weave material is attached to one surface of each of two layers of felt, and the non-backed felt surfaces are then coated with a mixture of rubber latex and an adhesive. These surfaces are firmly pressed together, the hessian is stripped off, and the felt is dried out to give a firm composite layer. J. W. B.

**Bonding Artificial Fibres to Rubber.** B.B. Chemical Co. Ltd. and T. C. Morris. *B.P.* 653,569.

Artificial fibres, e.g. viscose rayon or nylon, bond much more readily to rubber if they are first coated or impregnated with a permanently fusible, permanently soluble dihydroxybenzene–aldehyde resin. The effect of the treatment persists for a long time. C. O. C.

**Adhesive Coated Fabrics.** Johnson & Johnson (Great Britain) Ltd. *B.P.* 653,921.

The backing fabric is coated on one side with a normally tacky, pressure-sensitive adhesive, e.g. poly*iso*butylene, and on the other side with an elastomer incompatible with the first coating, e.g. a butadiene–acrylonitrile copolymer. C. O. C.

**Coated Non-woven Fabric.** Henry H. Frede & Co. Inc. *B.P.* 653,680.

A sheet of randomly distributed unwoven fibres is coated on both sides. The coating on at least one side consists of polyethylene glycol of mol. wt. 1000–2000 (25–65 parts) and a styrene–maleic anhydride interpolymer (75–35 parts) and has to be heated to 250–450°F. It is applied preferably as a 0·5–10·0% aq. soln. The product is highly absorptive, very flexible, and exceedingly soft and smooth. Even when wet it resists ordinary tearing stresses. C. O. C.

**Coating an Inorganic Fabric with Polytetrafluoroethylene.** du Pont and P. F. Sanders. *U.S.P.* 2,539,329.

Glass, asbestos, or metal woven fabric is thickly coated with an aqueous suspension of polytetrafluoroethylene and then dried. It is rolled or friction-calendered on unheated or moderately heated rollers, and then heated to at least the fusion temperature of the polymer. The coating is free from "mud cracks" (microscopic cracks due to shrinkage of the polymer) or surface checking. C. O. C.

**Cause of Damage to Natural Fibres by Micro-organisms—I.** W. Wegener and R. Questel. (VI, p. 352.)

**Sulphur Chloride Reactions in relation to the Rubber Industry.** C. E. Webb. (XIII, this page.)

## XI—PAPER AND OTHER CELLULOSIC PRODUCTS

**Structure and Properties of Cellulose, its Esters, and its Ethers. XXXII—Conditions for the Interconversion of Native and Hydrate Cellulose.** M. Ginzberg and Z. Rogovin. *J. Gen. Chem.* (*U.S.S.R.*), 21, 933–939 (May 1951).

Hydrate cellulose, formed by the regeneration of cellulose that has been swelled or dissolved by an aqueous alkaline medium, differs from native cellulose both in structure, as evidenced by the X-ray diffraction pattern, and also in physicochemical properties, such as hygroscopicity, dyeability, and susceptibility to hydrolysis by acids. All these properties were examined for various preparations of cellulose, and it was found that structural and physicochemical properties cannot always be correlated in this way. Thus, if cotton cellulose is regenerated from the trisodium deriv. formed by the action of metallic sodium dissolved in liquid ammonia, the product has the hydrate-cellulose structure, but in physicochemical properties is intermediate between native and typical hydrate cellulose (mercerised cotton). On the other hand, if mercerised cotton is heated to 230°C. in glycerol, its structure changes to that of native cellulose, but its physicochemical properties are not appreciably affected. A. E. S.

## XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

**Dyeing of Chrome Leather with Anionic Dyes.** G. Otto. (VIII, p. 354.)

## XIII—RUBBER; RESINS; PLASTICS

**Chemical Constitution of the Rubber Molecule.** S. S. Pickles. *Trans. Inst. Rubber Ind.*, **27**, 148–165 (June 1951).

A historical review of work on the constitution of rubber, with 51 references. C. O. C.

**Sulphur Chloride Reactions in relation to the Rubber Industry.** C. E. Webb. *Trans. Inst. Rubber Ind.*, **27**, 179–191 (June 1951).

The reaction between sulphur chloride and water and its consequences in cold-cure vulcanising are discussed. This is followed by an account of work on the reaction between sulphur chloride and rubber, with emphasis on the conditions favouring intermolecular and intramolecular reactions. Examples are given of factors accelerating deterioration of rubber vulcanised with sulphur chloride. Finally some miscellaneous reactions of sulphur chloride in relation to the rubber industry are discussed. 28 references. C. O. C.

**Polymers and Copolymers—Coating Compositions.** Monsanto Chemical Co. and G. R. Barrett. (III, p. 348.)

## XIV—ANALYSIS; TESTING; APPARATUS

**Differentiation of Ripe and Unripe or Dead Cotton.** P. A. Koch. *Textil-Rund.*, **6**, 169–175 (April 1951).

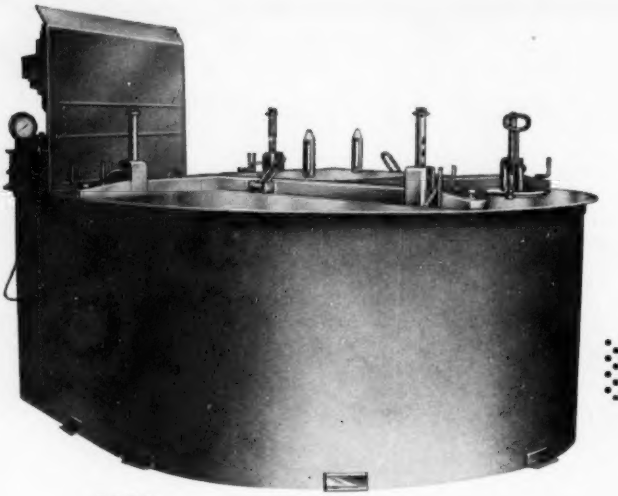
**Morphology of Regenerated Cellulose Fibres.** J. M. Preston and G. D. Joshi. *Kolloid-Z.*, **122**, 6–8 (April 1951).

A brief literature survey of the subject is first given; there are 30 references. Experiments are then reported in order to establish a suitable microscopic technique for the exact behaviour of the various fibre cross-sections, in view of the similarities between viscose and cellulose acetate fibres, and the differences between viscose and cuprammonium fibres. For this purpose the fibre cross-section is dyed with Sky Blue FF (*C.I.* 518), and a part of the coloured section then decolorised with cold 12% pyridine to afford a better contrast. H. H. H.

**Papyrographic Analysis of Polyamides and Polyurethan.** H. Zahn and H. Wolf. *Melliand Textilber.*, **32**, 317–321 (April 1951).

Nylon 66 and 610, Perlon L and U, and mixed condensates of caprolactam with 5% of adipic acid–hexamethylenediamine are differentiated by hydrolysis with hydrochloric acid. The products of hydrolysis, viz. hexamethylenediamine, ε-aminocaproic acid, adipic acid, and sebacic acid, are identified by papyrographic (paper-chromatographic) analysis. A mixture of *sec.*-butanol, formic acid, and water is employed for separating bases and amino acids, and dicarboxylic acids are separated by means of a mixture of *iso*butanol, glycol, and conc. ammonia. B. K.

**Turbidimetric Titration of Cellulose Acetate.** J. Bischoff and V. Desreux. (VI, p. 352.)



## FORTHCOMING MEETINGS OF THE SOCIETY—*continued*

### SCOTTISH SECTION

*All meetings at 7 p.m., St. Enoch Hotel, Glasgow*

| | |
|---|---|
| **1951** | |
| Tuesday 9th Oct. | Dr. G. T. Douglas. *The Dyeing of 'Ardil' and 'Ardil'/Cellulose Unions* |
| Tuesday 30th Oct. | J. G. Evans, Esq., M.Sc.Tech. *Some Aspects of Synthetic Fibres* |
| Tuesday 13th Nov. | Professor J. B. Speakman, D.Sc., F.R.I.C., F.T.I. Details later |
| Tuesday 11th Dec. | J. Boulton, Esq., M.Sc.Tech., F.R.I.C., F.T.I. *Rayon Staple: A Dyeing Miscellany* |

### BRADFORD JUNIOR BRANCH

*All meetings held in the Bradford Technical College at 7.15 p.m.*

| | |
|---|---|
| **1951** | |
| Friday 19th Oct. | Miss Esmee Smith (Wm. Smith & Co. Ltd.) *The Dyeing of Unions* |
| Wednesday 31st Oct. | Visit to Courtaulds Limited, Westcroft Mill, Bradford |
| Thursday 15th Nov. | FILM EVENING. (1) *Not Just Velvet* (Lister & Co. Ltd.) (further details later) |
| Monday 10th Dec. | Dr. G. H. Lister (Sandoz Products Ltd.) *Textile Auxiliaries in Relation to the Textile Industry* |
| **1952** | |
| Tuesday 22nd Jan. | STUDENTS' ANNUAL COMPETITION EVENING |
| Monday 18th Feb. | Dr. C. S. Whewell (Leeds University) *The Wet Finishing of Wool Textiles* |
| Thursday 28th Feb. | THE JUNIOR BRANCH DANCE at the Queen's Hall |
| Wednesday 5th March | J. A. Hepworth, Esq., B.Sc., A.T.I. (Shell Chemicals Ltd.) *Petroleum Derived Chemicals in the Textile Industry* |
| Saturday 8th March | Visit to Wool Industries Research Association, Torridon |
| Tuesday 25th March | E. E. Tallis, Esq., B.Sc., A.R.I.C. (Courtaulds Ltd.) *Recent Developments in Viscose Rayon and Staple Manufacture* |

There will be a visit to Salts (Saltaire) Ltd., the date of which has not yet been fixed.

### MANCHESTER JUNIOR BRANCH

*All meetings commence at 6.30 p.m.*

| | |
|---|---|
| **1951** | |
| Friday 26th Oct. | Two papers by (*a*) Dr. W. Shaw of the Calico Printers' Association Ltd.; (*b*) Mr. Sutton of T. E. Marchington & Co. Ltd. *Cellulose Acetate and Vat Dyes.* Reynold's Hall, College of Technology, Manchester |
| Wednesday 7th Nov. | Visit to Standfast Ltd., Lancaster. For details contact the Secretary, Manchester Junior Branch |
| Friday 16th Nov. | Two short papers by post graduate research students of the College of Technology. Titles and lecturers to be given later. Gas Showrooms, Manchester |
| **1952** | |
| Friday 11th Jan. | S. Burgess, Esq. and H. Hampson, Esq. *The Application of Vat Dyestuffs to Viscose Rayon Packages.* Reynold's Hall, College of Technology, Manchester |
| Friday 14th Mar. | Lecturer from the Bleachers' Association Ltd. Name later. *Progress in Textile Bleaching.* Reynold's Hall, College of Technology, Manchester |

### WEST RIDING SECTION

*All meetings held at the Great Northern Victoria Hotel, Bradford, at 7.15 p.m. unless otherwise stated*

| | |
|---|---|
| **1951** | |
| Friday 19th Oct. | SUPPER AND SMOKER |
| Thursday 8th Nov. | Dr. F. Happey (Head of Dept. of Textile Industries, Technical College, Bradford). *Synthetic and Natural Polypeptides* |
| Thursday 22nd Nov. | C. C. Wilcock, Esq., F.T.I., A.R.T.C., and R. A. McFarlane, Esq. (Courtaulds Ltd.) *Some Comments on the Winch Dyeing of Rayon Fabrics* |
| Tuesday 27th Nov. | Professor W. Bradley. Title later. Metropole Hotel. Leeds |
| Thursday 6th Dec. | Dr. G. T. Douglas (I.C.I. Ltd.). *The Dyeing of 'Ardil' and 'Ardil' Cellulose Unions* |
| **1952** | |
| Friday 18th Jan. | LADIES' EVENING |

# SITUATIONS VACANT AND WANTED, Etc.

Replies may be addressed "Box —, Society of Dyers and Colourists," OCEAN CHAMBERS, 32–34 PICCADILLY, BRADFORD, YORKS., where all communications relating to these Advertisements, which are treated in strict confidence, should be addressed.

The Publications Committee is prepared to receive Advertisements relating to SITUATIONS VACANT, SITUATIONS WANTED, or MISCELLANEOUS ITEMS for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to the General Secretary, The Society of Dyers and Colourists, OCEAN CHAMBERS, 32–34 PICCADILLY, BRADFORD, YORKS.

## SITUATIONS VACANT

COLOUR CHEMIST with good experience in roller or screen printing required as assistant to manager of progressive screen print works. Reply giving details of age, education, technical experience, and salary required to Box V524

LARGE Dyestuff Manufacturers in Manchester area urgently require honours chemistry graduates, with or without experience, for technical service work in the dyehouse laboratories. Excellent prospects and staff pension scheme. Reply Box V528

APPLICATIONS are invited from suitable candidates for the post of DIRECTOR in the Grade of Rs.2000–100–2500 per mensem. This being a position of vast responsibility requires not only a man of highest professional and organisational ability, capable of directing Physico-Chemical and Technological research, but also one with personality of inspiring leadership. As head of the institute he will be responsible for the administration, research and public relations with Government, Industry and Scientific Institutions. A certain background of textile technology is preferable but not essential. Selected candidate will receive D.A., benefits of Provident Fund as per prevailing rules and bungalow at preferred rates. Applications with full particulars should reach the Secretary, The Ahmedabad Textile Industry's Research Association, Post Box No. 170, Ahmedabad, India, not later than 31st October 1951.

WORKS CHEMIST preferably with experience of Anthraquinone Dyestuffs, required by old-established Company. Applications giving age, qualifications and experience should be addressed to—The Managing Director, The Yorkshire Dyeware & Chemical Co. Limited, Leeds 10.

A well-known Midlands organisation of Dyers and Finishers invite applications for the position of Manager of their screen printing department. Applicants must not only be efficiently technically equipped, but must be capable of controlling and organising the whole department. The salary offered will be such as to attract a competent man, and suitable accommodation will be found. Applications, which will be treated with the utmost confidence, should be directed in the first instance to—Box V532.

THE HOSIERY AND ALLIED TRADES RESEARCH ASSOCIATION

Thorneywood House, 4 First Avenue, Sherwood Rise, Nottingham

TWO Chemists are required for research on problems relating to the dyeing and finishing of knitted products. An honours degree in chemistry is essential and textile experience would be considered an additional advantage. The posts are open to both men and women.

The successful candidates will work in the Association's laboratories in Nottingham. The minimum salary offered is £670, but an appreciable higher commencing salary will be paid for outstanding qualifications and/or experience. Both posts are progressive and carry benefits under the F.S.S.U. Scheme.

Forms of application, which should be completed and returned by 9th October, 1951, may be obtained from the Secretary, Mr. N. F. Cooper, at the above address who will also be willing to supply additional information concerning the posts.

### Situations Vacant—*continued*

MANAGER required for Dyestuffs and Intermediates Department of old-established London firm representing important Continental manufacturers. Applicant should be fully experienced in sale of Dyestuffs to U.K. consumers, and to U.K. firms selling abroad. Write in confidence Box J.W. Harwood Press (Advertising) Ltd., 47 West Street, Harrow, Middlesex.

## SITUATIONS WANTED

MEMBER, Dyeing and Textile Chemistry Diploma, Full Technological Certificate in Dyeing of Textiles; yearly experience in dyehouse, sound knowledge of laboratory work, seeks employment, home or abroad Box W529

MEMBER (24) seeks employment as assistant to manager or any progressive appointment. Some experience in woollen manufacture. Diploma in Textile Industries, Leeds University. Box W530

MANAGER— Aged 40 years, desires change. 20 years' experience in the dyeing and finishing of cotton and rayon piece goods with well-known firm. Full technical qualifications. Box W531

## MISCELLANEOUS

ON SALE IN ULSTER

ONE combined Skim and Back Starching Machine comprising steam heated cylinder 12' 0" dia. × 5' 6" on face, working steam pressure 30 lb. P.S.I. 5 Copper cylinders 56½" on face × 28" dia. are mounted on vertical trees with patent dollheads suitable for 10 lb. P.S.I. This machine is complete with Mather & Platt Filling Machine and driven by electric motor (not included) with inverted tooth reduction gear and internal expanding clutches, cone pulleys and shafting. In splendid order. Apply Box M527

THE proprietors of British patents No. 598,985 for "Improvements in or relating to the Manufacture of Azo Dyestuffs", No. 602,104 for "Acylacetylated Derivatives of Aryl Amines", No. 602,347 for "Improvements in and relating to Poly-azo-dyestuffs" and No. 598,260 for "Process for the Production of Coloured Discharges on Dyed Fabrics and Products thereof" are prepared to enter into negotiations for the SALE of the patents or for the grant of a LICENCE thereunder. Enquiries to be addressed to Carpmaels & Ransford, 24 Southampton Buildings, Chancery Lane, London W.C.2

WANTED— A Smith's Rotary Drum, capacity approx. 200 lb. A three bed press for ladies' hosiery approx. 78 in. × 42 in. Both must be in good condition, preferably located in Northern Ireland. Replies to Box M533

TRANSLATION offered of any Russian article abstracted in the Journal. Apply to Dr. A. E. Stubbs, "Ashbourne", Radcliffe Road, Bolton, Lancashire.

WANTED— Copy of bound volume on Symposium on Fibrous Proteins. Address Box M448

## MEMBERS' CHANGES OF ADDRESS

Archer, G., formerly of Bradford, to Flat 8, 20 Bermers Street, Peterson Road, Wakefield

Backhouse, A. J., formerly of Leeds, to "Rockleigh", Park Road, Stroud, Glos.

Brassard, H. A, formerly of London, to Seaden, Easton Bavents, Southwold, Suffolk

Callaway, R. D., formerly of Wilsden, to 96 St. Enoch's Road, Wibsey, Bradford

Carlene, Dr. P. W., formerly of Wilmslow, to c/o Fibres Technical Service and Development Dept., Plastics Division, I.C.I. Ltd., The Hall, Welwyn, Herts.

Catlow, J., formerly of Manchester, to 18 Alma Road, Heaton Moor, Stockport

Costandius, P., formerly of Manchester, to c/o Berg River Textile Ltd., P.O. Box 306, Paarl, Cape Province, South Africa

Ferguson, T. D., formerly of North Carolina, to P.O. Box 106, Altavista, Virgina, U.S.A.

Gewing, M., formerly of Eglantine Gardens, to 9 Rosemary Park, Upper Malone, Belfast

Hexton, F. W., formerly of 261 Hyde Park Road, to 32 Kelso Road, Leeds 2

Makarewicz, C., formerly of 31 Dryden Street, to 55 Cranmer Street, Nottingham

McWhinney, M., formerly of Holme Lane, to "Stone Haw", Church Road, Sutton-in-Craven, near Keighley

Moores, E., formerly of Congleton, to Gleddenhurst, Coppice Road, Poynton, Cheshire

Moore, G., formerly of West-Bowling, to 20 Welwyn Avenue, Wrose, Shipley

Priest, E., formerly of Leeds 10, to 29 Church Road, Arley, near Coventry

Rankin, J., formerly of Bolton, to 30 Moorside Road, Eccleshill, Bradford

Richardson, G. G., formerly of London E.14, to c/o Nathan Cohen & Sons Ltd., Peak Works, Alfred's Way, By Pass Road, Barking, Essex

Schewitz, D., formerly of Boom Street, to Box 10, Belgravia, Johannesburg, South Africa

Schlaeppi, F., formerly of New York, to c/o Ciba Co. Ltd., 1235 McGill College Avenue, Montreal, Quebec, Canada

Silva, M. A. da, formerly of 21 Grove Lane, to c/o Dyeing & Colour Chemistry Department, Leeds University.

Smyth, J. E., formerly of Belfast, to Ballievay, Banbridge, Co. Down

Subramaniam, C. R., formerly of 50/18 Mayura Place, to 50/5 Mayura Place, Havelock Road, Colombo, Ceylon

Taylor, H. W., formerly of 33 Lenham Road, to 10 Milton Avenue, Sutton, Surrey

Wilkie, J., formerly of Glasgow S.W.1, to 22 Merryton Avenue, Giffnock, Renfrewshire

Winkler, A., formerly of Leeds, to 251 Yews Hill Road, Lockwood, Huddersfield

CHEMICALS IN INDUSTRY
PYRIDINE
NAPHTHALENE
XYLOL
SODIUM CHLORATE
SULPHURIC ACID
SALT
ANILINE
HYDROCHLORIC ACID
CAUSTIC SODA
STAVELEY

PUBLISHED FOR THE SOCIETY AND PRINTED BY CHORLEY AND PICKERSGILL LTD LEEDS
ENTERED AT THE NEW YORK POST OFFICE AS SECOND CLASS MATTER